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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

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VOLUME XII. 1854.

360346
24. 1. 39.

LONDON:
PUBLISHED BY TAYLOR AND FRANCIS,
RED LION COURT, FLEET STREET.

PRINTED BY TAYLOR AND FRANCIS,
RED LION COURT, FLEET STREET.

THE

CHEMICAL GAZETTE.

No. CCLXIX.—January 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Saponine. *By* F. Rochleder *and* R. Schwartz.

Saponine was first found in the root of *Saponaria officinalis*. Bley afterwards discovered a peculiar substance in the root of *Gypsophila Struthium*, which he named *struthiine*. Bussy ascertained the identity of struthiine with saponine. Fremy has instituted experiments to ascertain the composition of saponine. The numbers which he obtained by analysis agree with the formula $C^{26} H^{24} O^{16}$ or $C^{24} H^{21} O^{15}$. Fremy also discovered a substance in the fruit of the horse-chestnut, which was readily soluble in water, and dissolved in alcohol with a degree of difficulty which increased in an inverse proportion to the quantity of water contained in that fluid; it was insoluble in æther; its watery solution frothed strongly, and when heated in presence of acids became converted into an acid, which is insoluble in water, and separated in the form of white flakes. This acid, which according to Fremy furnishes crystallized salts with alkalies, and which is also formed by the action of alkalies upon the substance obtained from the horse-chestnut, was named by him *æsculic acid.*

As the degree of solubility of saponine in water, alcohol, and æther is the same as that of the substance obtained from the horse-chestnut, and as the frothing watery solution of saponine, when heated after the addition of a mineral acid, is also decomposed with separation of white flakes, Fremy has regarded the substance obtained from horse-chestnuts as identical with saponine. Fremy gives for æsculic acid the formula $C^{52} H^{46} O^{24} = 2(C^{26} H^{24} O^{16}$ saponine $- H^2 O^2) - O^4$. As the authors did not succeed in preparing from saponine an acid possessing the properties of Fremy's æsculic acid, either the principle of the horse-chestnut is not saponine, or the statements with respect to æsculic acid must be erroneous; which of these alternatives is correct can only be ascertained by experiment.

Saponine has also been recognized in the root of *Gypsophila fastigiata*, L., *G. altissima*, L., and *G. acutifolia*, Fisch. Malapert found saponine in *Dianthus caryophyllus*, L., *D. Carthusianorum*, L., *D. cæsius*, L., *D. prolifer*, L.; in *Silene inflata*, L.; in all parts of

Silene nutans, L., except the seed; in *Lychnis calcedonica*, L., *L. Flos Cuculi*, L., and the root of *L. vespertina*, Sibth.; also in the root and seed of *Agrostemma Githago*, L. According to Le Beuf, there is a large quantity of saponine in the bark of *Quillaja saponaria*. From Malapert's experiments, it appears that saponine is also contained in *Anagallis arvensis*, L., and *A. cærulea*, Schreb. Saponine may perhaps also occur in the fruit of *Pircunia abyssinica*, and in many *Sapindaceæ* and *Mimoseæ*, and may consequently be a principle widely distributed in the vegetable kingdom.

Saponine was prepared by the authors in the following manner:—The root of the *Gypsophila* was cut in pieces, and decocted with alcohol of spec. grav. 0·828; the solution was filtered whilst boiling-hot, and left standing for twenty-four hours in a cool place, during which period a white deposit of saponine was formed; this was collected on a filter, well washed with alcohol to which æther had been added, and then dried at 212° F. Saponine thus prepared has the properties attributed to this substance in the manuals: it is colourless, readily soluble in water, forming a frothing fluid; soluble with difficulty in cold, more readily in hot alcohol; insoluble in æther. Its powder is violently provocative of sneezing. The watery solution, when mixed with muriatic or sulphuric acid and heated to boiling, furnishes a flocculent precipitate, insoluble in water, but soluble in alcohol, and possessing neither colour nor odour. The watery solution of saponine, when mixed with solution of sugar of lead, furnishes a gelatinous precipitate; when the fluid filtered from this is heated to boiling, a fresh white precipitate, somewhat less gelatinous than the former, is produced; this, however, when washed on the filter, swells up, and becomes gelatinous and transparent. Analyses of saponine, dried at 212° F., gave,—

Carbon	52·45	52·55	52·63	24 =	144	52·17
Hydrogen ..	7·30	7·03	7·48	20	20	7·24
Oxygen	40·25	40·42	39·89	14	112	40·59

The cause of the amount of carbon being too high is the presence of a small quantity of a resinous body, which is difficult to get rid of, and also of a trace of a product of the decomposition of saponine, which is richer in carbon and poorer in oxygen than that substance, but contains exactly the same quantity of hydrogen.

When some muriatic or sulphuric acid is added to the watery solution of saponine, and the whole is heated to boiling, it becomes turbid in a few moments, and a flocculent precipitate, of a white or pale yellowish colour and a gelatinous consistence, is produced; this is separated from the fluid after cooling by filtration. The best mode of obtaining this substance in a state of purity is to dissolve it in boiling acetic acid, to filter the solution whilst boiling, and to mix the filtrate with water and allow it to cool. White flakes are separated, which are collected upon a filter and washed with water. After drying for several hours at 248°–257° F., the analysis of this substance gave the following results:—

Carbon	63·35	12 =	72	63·16
Hydrogen	8·57	10	10	8·77
Oxygen	28·08	4	32	28·07

A portion of the substance, prepared in the same manner, but dried for twenty-four hours at 212° F., gave the following numbers on analysis:—

Carbon	67·04	60 =	360	67·41
Hydrogen	8·88	46	46	8·61
Oxygen.....	24·08	16	128	23·98

From this we get $C^{12} H^{10} O^4 = C^{12} H^9 O^3 + HO$. $C^{60} H^{46} O^{16} = 5(C^{12} H^9 O^3) + HO$; and this composition, the insolubility of the substance in water, its solubility in alcohol and boiling acetic acid, its behaviour during dry distillation, its property of dissolving in moderately concentrated sulphuric acid with a red, and in concentrated acid with a yellowish-brown colour, and of furnishing with alkalies and earths bitter compounds soluble in water, show that it is identical with chinovic acid or with chinova bitter.

The fluid from which this substance has been deposited holds in solution, together with the free sulphuric or muriatic acid employed in the decomposition of the saponine, an organic substance. Carbonate of lead or hydrated oxide of lead is added to this fluid, which is then filtered from the sulphate or basic chloride of lead formed, mixed with a little liquid sulphuretted hydrogen, filtered from the scanty precipitate of sulphuret of lead, and treated with animal charcoal. On evaporation, it furnishes a yellowish-brown residue, with a nauseous taste, which is readily soluble in water, and which, when dried at 212° F., gave the following numbers on analysis:—

Carbon	41·99	12 =	72	42·10
Hydrogen	6·55	11	11	6·44
Oxygen	51·46	11	88	51·46

If the composition of saponine be compared with that of its products of decomposition, the following simple equation is obtained:—

$C^{24} H^{20} O^{14}$ saponine $= C^{12} H^9 O^3$, chinovic acid $+ C^{12} H^{11} O^{11}$ hydrate of carbon.

Caincic acid has the composition $C^{16} H^{13} O^7$; it splits, like saponine, into chinovic acid and a hydrate of carbon, when its watery solution is treated with acids at an elevated temperature. The quantities of chinovic acid and hydrate of carbon contained in the two conjugate compounds differ; saponine contains equal equivalents of both, whilst in caincic acid the quantity of chinovic acid is three times as large for the same quantity of hydrate of carbon:—

$3C^{16} H^{13} O^7$ caincic acid $= C^{48} H^{39} O^{21} = 3(C^{12} H^9 O^3)$ chinovic acid $+ C^{12} H^{10} O^{10}$ hydrate of carbon $+ 2HO$.

$C^{24} H^{20} O^{14}$ saponine $= \ldots = C^{12} H^9 O^3$ chinovic acid $+ C^{12} H^{10} O^{10}$ hydrate of carbon $+ HO$.

Two other substances are contained in the root with the saponine, which in a different method of preparation of that principle might render it impure, and lead to false results in analysis. The root is

extracted with alcohol, the boiling solution filtered, and the saponine separated by filtration; the filtrate is then precipitated by solution of sugar of lead, the white precipitate produced removed by filtration, and the fluid freed from lead by sulphuretted hydrogen; if the filtered fluid is then evaporated on the water-bath to the consistence of a syrup, and the residue mixed with anhydrous alcohol, a flocculent precipitate of a white colour is formed, which, when washed with alcohol and dried at 212° F., constitutes a white powder of a sweet taste, which gave the following numbers on analysis:—

Carbon	42·24	12 =	72	42·10
Hydrogen	6·76	11	11	6·44
Oxygen	51·00	11	88	51·46

This substance is a mixture of gum and sugar, of which the former is insoluble, the latter soluble only with great difficulty, in anhydrous alcohol. Hence, therefore, when the root is extracted with weak alcohol, and the fluid afterwards precipitated by strong alcohol, the saponine obtained is always contaminated with gum or sugar.

Saponine is decomposed by weaker acids in the same manner as by sulphuric or muriatic acid. In endeavouring to purify saponine by dissolving it in a mixture of boiling alcohol and acetic acid, a saponine was obtained, which on analysis gave quite different numbers from those furnished by the previous samples:—

Carbon	59·70	60 =	360	60·00
Hydrogen.....	7·99	48	48	8·00
Oxygen.....	32·31	24	192	32·00

A portion of the saponine is therefore converted by this treatment into chinovic acid and sugar, for the preceding numbers agree with a mixture of saponine and chinovic acid:—

$C^{60}H^{48}O^{24} = C^{24}H^{20}O^{14}$ saponine $+ 3(C^{12}H^{9}O^{3})$ chinovic acid $+ HO$.

A second treatment in the same manner gave,—

Carbon	55·69	55·56	55·32	36 =	216	55·38
Hydrogen ..	7·77	7·47	7·79	30	30	7·69
Oxygen	36·54	36·97	36·89	18	144	36·93

All the three analyses were performed with substances prepared at different times. They represent the following relation:—

$C^{36}H^{30}O^{18} = C^{24}H^{20}O^{14}$ saponine $+ C^{12}H^{9}O^{3}$ chinovic acid $+ HO$.

A portion of saponine, boiled for a longer time with acetic acid and alcohol, gave the following composition:—

Carbon	62·42	12 =	72	63·16
Hydrogen	9·04	10	10	8·77
Oxygen	28·54	4	32	28·07

The saponine was therefore nearly completely resolved into chinovic acid and hydrate of carbon.

According to these investigations, saponine is allied to æsculine and other bitter principles, the greater number of which have been ascertained to be conjugate compounds of a hydrate of carbon —. *Sitzungsb. der Akad. der Wiss. zu Wien*, 1853, p. 334.

On the Behaviour of Creosote with Lime at a high Temperature.
By C. Völckel.

When pure anhydrous creosote is mixed with finely-pounded, freshly-calcined lime, no heat is evolved, and indeed no action is perceptible. On the application of heat, a colourless fluid first passes over at the boiling-point of the creosote; this is pure unchanged creosote. When the temperature is raised, the creosote combined with the lime is decomposed. When heated on the open fire, a yellow oleaginous fluid distils over in small quantity, whilst the residue in the retort becomes blacker and blacker. Towards the end of the distillation, combustible gases are evolved, which burn with a strongly luminous flame.

The yellow distillate was first heated on the water-bath. A few drops of a colourless fluid pass over; it has an odour like acetone. The remaining fluid was agitated with solution of potash, in order to remove any creosote which might have passed over unchanged, and then distilled with water. The oleaginous fluid which distils over is of a pale yellowish colour. It has an aromatic odour and a burning taste. It is insoluble in water, readily soluble in alcohol and æther, and burns with a very luminous reddish flame. The specific gravity of the substance, deprived of water over chloride of calcium, is 0·976 at 68° F.

This fluid begins to boil at 248° F. The boiling-point however suddenly rises to 356° F. Between this temperature and 392° F. the greater part of the fluid passes over; it still retains a slight yellowish colour. Above 392° F. a few drops of a fluid still pass over; this has nearly the same specific gravity as water, possesses the same odour as capnomor, and may perhaps be that substance.

For analysis, the fluid which passed over between 356° and 392° F. was divided into two portions:—

I. 0·192 grm. of the first portion, which passed over between 356° and 374° F., gave 0·548 grm. of carbonic acid and 0·147 grm. of water.

II. 0·343 grm. of the second portion, passing over between 374° and 392° F., gave 0·996 grm. of carbonic acid and 0·266 grm. of water. This gives—

	I.	II.
Carbon	77·72	79·16
Hydrogen	8·49	8·60
Oxygen	13·79	12·24

From this it follows that the fluid which passes over between 356° and 392° F. contains several products of the decomposition of creosote. The small quantity of it however (100 grms. of creosote, distilled with an equal weight of lime, furnished only 10 grms.) allowed no further separation. This fluid has much resemblance to that which Reichenbach has described under the name of capnomor. It dissolves readily in concentrated acetic acid; it is again separated unchanged by water. Concentrated nitric acid attacks it very violently even at the ordinary temperature. It dissolves in concen-

trated sulphuric acid with a brown colour; heat is evolved during the process, and a conjugate sulphuric acid is formed.

These products of the decomposition of creosote also occur amongst the products of the distillation of wood. They are also contained in the light tar-oil, which is the first to pass over during the distillation of tar, and likewise in the heavy tar-oil which follows this.

The occurrence of this product of the decomposition of creosote in light tar-oil is the reason why light tar-oil, which has only been purified by caustic potash, always furnishes on analysis less hydrogen than would agree with a mixture of oxide of mesityle, $C^6 H^5 O$, and mesitylene, $C^6 H^4$.

These oleaginous fluids dissolve with the creosote in concentrated solution of potash. The addition of water separates a portion of them; complete separation however is only effected after long boiling.

Commercial creosote, therefore, when it has not been purified by the process described in my memoir*, always contains more or less of these products of decomposition. The specific gravity of this impure creosote will be less than that found by me for pure creosote, 1·076. Its analysis will furnish a greater amount of carbon and hydrogen than that of pure creosote. It was a creosote of this description that was investigated by Von Gorup-Besanez†; this appears from his description of the behaviour of creosote, especially towards acetic acid and lime. According to Von Gorup-Besanez, the creosote analysed by him only dissolved partially in ordinary acetic acid.

Pure creosote however is very readily and completely dissolved, not only by concentrated, but also by ordinary acetic acid. A solution of it in an excess of acetic acid, may be mixed with water without producing any turbidity. Now as the above-described products of the decomposition of creosote, as well as capnomor, are soluble only in concentrated, and not in ordinary acetic acid, a sample of creosote contaminated with these substances will only be partially soluble in the ordinary acid. The solubility of creosote in common acetic acid, and in very dilute solution of potash, may consequently be regarded a characteristic of purity.

According to Von Gorup-Besanez, when creosote is mixed with lime, heat is evolved, and the mixture acquires colour. During distillation, a milky fluid passes over at 212° F.; between 356° and 374° F., an aromatic fluid, which floats upon water; and as soon as the temperature reaches 397° F., a heavy oil. The evolution of heat observed by Von Gorup-Besanez on mixing the creosote and lime, arose perhaps from the creosote employed containing some water. The fluid passing over at 406° F. also most probably existed ready formed in the creosote, for the compounds of creosote with bases are only decomposed at a temperature above the boiling-point of creosote.

* Ann. der Chem. und Pharm., lxxxvi. p. 66. † *Ibid.*, p. 223.

Von Gorup-Besanez analysed the oil which passed over between 397° and 406° F., but without freeing it, by treatment with solution of potash, from the creosote which always goes over with it. The numbers found by him fall between the analyses I. and II. of the products of the decomposition of creosote by lime, given in the former part of this memoir.

Although creosote is a readily convertible substance, I have not succeeded any better than Von Gorup-Besanez in obtaining well-characterized products of decomposition. I have not investigated the behaviour of creosote with chlorate of potash and muriatic acid.

Creosote, as has already been observed, is changed even by heat. After every distillation of a considerable quantity of creosote, a residue of a dark colour is left; this contains resins similar to those obtained by Von Gorup-Besanez by the action of oxide of silver upon creosote. These resins also occur in wood-tar.

Von Gorup-Besanez did not succeed in obtaining a constant lead compound with creosote. The lead compound analysed by me was obtained by the precipitation of a dilute ammoniacal solution of creosote with a dilute solution of acetate of lead mixed with ammonia.

Creosote dissolves with difficulty in dilute ammonia, but pretty readily in ammonia of the usual strength; the combination of creosote with ammonia is more rapidly effected when the creosote is first dissolved in several times its volume of alcohol.

A solution of creosote in ammonia becomes coloured when exposed to the air. In order therefore to effect the solution of the creosote as rapidly as possible for the preparation of the lead compound for analysis, a small quantity of creosote, 1 or 2 grms., was dissolved in 6 or 8 grms. of absolute alcohol, then mixed with concentrated ammonia, and diluted with 100 to 200 grms. of water. This dilute solution gives a white precipitate with an equally dilute solution of acetate of lead to which ammonia has been added. The lead compound thus obtained had always the same composition.

From the experiments of Von Gorup-Besanez, it also appears that the substances described by Reichenbach as picamar and cedriret were not contained in the creosote examined by him; for the creosote completely distilled over at 428° F., like that which was used in my investigations. Consequently had picamar been present, its boiling-point being according to Reichenbach 518° F., the creosote must also have reached this point before it could have passed over. Von Gorup-Besanez must also have observed the formation of cedriret during the action of chromate of potash and sulphuric acid upon creosote.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 306.

On the Acids contained in certain Fungi. *By* M. Dessaignes.

The author refers to the researches of Braconnot, who discovered two acids, *boletic* and *fungic acids*, in fungi; and also to those of Bolley*.

He obtained boletic acid from the *Boletus pseudo-igniarius*, the

* Chem. Gaz., vol. xi. p. 291.

fungus in which this acid was discovered by Braconnot, and also in small quantity from the *Amanita muscaria* and the *Agaricus necator*. From his comparative examination of this acid and fumaric acid, he feels no doubt of their perfect identity. The analysis of dried boletic acid, effected by combustion *in vacuo* with oxide of copper and oxygen, gave C 41·85, H 3·73. Calculation from the formula $C^8 H^8 O^8$, which is that of fumaric acid, gives C 41·38, H 3·45. Boletate of silver, dried at 212° F., and then calcined, left 65·01 per cent. of silver; theory requires 65·45.

The crude acid obtained from the three fungi above mentioned, from which the boletic acid has been removed by concentration and crystallization, was neutralized by ammonia, and then precipitated by chloride of calcium; in this manner a considerable portion of phosphate of lime was produced. The filtered liquid was heated, when a white crystalline powder was suddenly precipitated. This salt of lime was washed and dissolved in weak nitric acid; the solution furnished no crystals; it was precipitated by acetate of lead. The lead salt did not crystallize. It was boiled several times in water, which extracted a small quantity of a soluble lead salt. The portion insoluble in boiling water was decomposed by sulphuretted hydrogen; the liquid filtered from the sulphuret of lead gave on evaporation concentric groups of prisms, which in the course of a few days became converted into large isolated crystals. These crystals burnt without leaving any residue. All their chemical properties agree with those of citric acid; the silver salt, dried at 212° F., was burnt with oxide of copper, and the silver determined in the form of chloride. The analysis of 100 parts of the salt gave,—C 13·96, H 1·21, Ag 62·67. Calculation from the formula of citrate of silver, $C^{12} H^{10} O^{14}$, 3Ag, gives,—C 14·03, H 0·98, Ag 63·15.

The fluid from which the citrate of lime had been precipitated by heat was treated with acetate of lead, and then with subacetate of lead, to extract the fungic acid. The greater part of the lead salt crystallized when left in a hot place. The crystals were separated by decantation from a lighter non-crystalline powder; from the crystals an uncrystallizable acid was obtained by means of sulphuretted hydrogen; this was half-saturated with ammonia, and in this manner a salt was obtained, crystallizing in the same form as the bimalate of ammonia, and which was readily purified by crystallization. From the aqueous solution of this salt, acetate of lead precipitated a crystallized lead salt, from which sulphuretted hydrogen separates a colourless acid, which crystallizes *in vacuo* in a confused manner, and deliquesces. This acid presents all the characters of malic acid. When heated for a long time in a tube closed at one end, it is converted into fumaric acid. Nearly neutralized by lime, and then heated to boiling, it deposits a pulverulent lime salt, which, when dissolved in weak nitric acid, furnished crystals similar to those of bimalate of lime. The bimalate of ammonia, heated to 356° F., also produced this sparingly soluble substance, which furnished bimalate of ammonia when treated in the same manner. The silver salt, dried at 212° F., was analysed, and gave,—C 13·59,

H 1·58, Ag 62·13. Calculation from the formula of malate of silver, $C^8 H^8 O^{10}$, 2Ag, gives C 13·79, H 1·15, Ag 62·07.

Fungic acid consequently appears only to be malic acid mixed with citric and phosphoric acids.—*Comptes Rendus*, November 21, 1853, p. 782.

On the Nutritive Value of Rape-Cake. By Prof. Emil Wolff.

The author in his experiments readily obtained $\frac{3}{4}$ths of a pound of milk with 1 lb. of rape-cake; it has however been ascertained, that under other circumstances, especially with cows of higher milk-producing power, this result had risen considerably; so that 1 lb. of rape-cake will produce, according to circumstances, between $\frac{1}{2}$ and $1\frac{1}{2}$ lb. of milk of very good quality, or on an average 1 lb. of milk. The quality of the milk bears reference only to the quantity of butter contained in it. The butter itself acquires a bad taste when the cow has been very plentifully fed with rape-cake; and as a general rule, 2 lbs. a day per head, which quantity was observed to produce the highest effect, is regarded as too much, if it be desired to obtain well-tasted butter. But when the milk is to be sold as such, a daily allowance of 2 lbs. of rape-cake is never too much; and the milk will then taste better in proportion as the other food is rich in non-nitrogenous nourishment and poor in proteine compounds.

In the production of milk, 1 lb. of rape-cake cannot be replaced by 2 lbs. of hay; for the purpose of maintaining an average living weight, in cows as well as in sheep, 1 lb. of rape-cake must be regarded as at least equal to 2 lbs. of hay; in many cases, especially when rape-cake is given in very small quantity with foods very poor in nitrogen (straw, potatoes, turnips, &c.), the equivalent of the rape-cake rises considerably, and the same nutritive effect is often obtained with 1 lb. of rape-cake as with 3 lbs. of hay.

The production of flesh is forwarded in as high a degree by feeding with rape-cake as by any other food. The author has observed the greatest effect to be produced with cows which were at their medium living weight, and which, during their highest production of milk, had been accustomed to a tolerably plentiful daily allowance of rape-cake. When these cows were deprived of the entire quantity of rape-cake, they rapidly fell to a considerable extent, but rose again regularly as soon as the daily allowance of 2 lbs. of rape-cake was restored to them. In this manner an increase of weight of 62 lbs. was produced in two cows in fourteen days; and this was obtained with 56 lbs. of rape-cake, so that 1 lb. of this substance effects an increase of fully 1 lb. in the living weight. After this the weight of the animals with the same diet remained pretty constant. From this it appears that with cows 1 lb. of rape-cake daily will gradually produce, and afterwards maintain an increase of 15 lbs. in the weight of the animal. This rapid and considerable effect of the rape-cake was only possible under the peculiarly favourable circumstances for the production of flesh existing in the present instance. Had the daily allowance of rape-cake been raised to 3 or 4 lbs. per

head, the weight of the animal would also gradually have risen to a corresponding extent; but this would hardly have been attained in so short a time, for the nearer the animal is completely fattened, the more slowly does it acquire weight, especially under the influence of the same food.

With sheep, 1 lb. of rape-cake in the daily food, supposing the whole quantity given to the animal to be composed of proper nourishment, produces gradually a weight of 20 lbs., at least in the first period of fattening, and afterwards apparently something less. The poorer the other food is in nitrogenous constituents, the more rape-cake may be given to the animal with good effect, and without giving cause to fear the production of meat of bad quality; nevertheless it does not appear to be advisable to raise the daily allowance of rape-cake above $\frac{2}{3}$ds of a lb. If a sheep of average weight be fed daily with about 4 lbs. of beet-root and $1\frac{1}{2}$ lb. of hay, together with a quantity of rape-cake, at first small, but gradually rising till it reaches $\frac{2}{3}$rds of a pound, the weight of the animal will be increased, in from six to eight weeks, according to circumstances, to an average extent of about 13 lbs.; these 13 lbs. will have been produced by 28 or 30 lbs. of rape-cake, which the animal would consume in that time.

The favourable influence of the rape-cake on the quality of the manure produced during the fattening is worthy of a high degree of consideration, as rape-cakes are of all cattle foods the richest in nitrogen; and the presence of nitrogen in manure constitutes its highest value. The author has ascertained, by the direct examination of sheep's dung, that by far the greater part of the nitrogen of the rape-cake passes into the dung, and is also retained in it for a considerable time during its accumulation in the stall, if the dung remains tolerably moist, in consequence of the greater quantity of water taken by the animal as a result of the nature of its food, or if it be moistened from time to time with water. When the rape-cake is given to the sheep in smaller quantity, during the winter feeding, so as merely to keep the animal at an average living weight without fattening, it may be assumed with certainty that only $\frac{1}{6}$th of the original quantity of nitrogen is lost in the process of nutrition and by decomposition in the stall; $\frac{5}{6}$ths of the value of the rape-cake as a manure are consequently retained in the dung produced. If such an improvement of the manure may thus be ascertained to be the effect of feeding sheep upon rape-cake, the quality of cattle manure is not less improved by similar nourishment; 1 lb. of rape-cake produces on an average 1 lb. of milk; this however only contains $\frac{1}{8}$th part of the nitrogen contained in the rape-cake, so that $\frac{7}{8}$ths of the nitrogen of the latter must pass into the dung; and this nitrogen will be retained more readily than in sheep's dung, as cow's dung is so much wetter and colder, and consequently undergoes a more gradual decomposition.

When rape-cake is employed in larger quantity for fattening, besides this loss in nitrogen, which on the average only reaches $\frac{1}{6}$th, or at the outside $\frac{1}{5}$th, a larger or smaller quantity will be retained

from the dung, according as the increase in the weight of the animal goes on faster or slower. The quantity of nitrogen fixed in the body during an increase, say of 100 lbs., in weight, cannot be determined with certainty; Boussingault's statement, however, that 3·66 lbs. of nitrogen are to be calculated for an increase of 100 lbs. in the living weight during fattening, appears to be too high in comparison with the quantity of nitrogen in the substance of an animal. Nevertheless, the author employs this statement as the basis of the following calculation, as no other observations have hitherto been made on this subject. In certain cases it appears that nearly the whole of the nitrogen contained in the rape-cake may be appropriated to the formation of flesh and milk; thus, such a case was, when in fourteen days (from March 27 to April 9) an increase in the living weight of two cows of 62 lbs. and 38 lbs. of milk was produced with 56 lbs. of rape-cake. These 56 lbs. of rape-cake contained 2·8 lbs. of nitrogen, whilst the flesh and milk produced under their influence contained 2·49 lbs. of that element; as soon, however, as the living weight corresponding to a certain mode of feeding is attained, and remains constant, only $\frac{1}{8}$th of the nitrogen of the rape-cake is fixed in the milk, whilst $\frac{7}{8}$ths pass off in the dung. If a longer period of fattening be adopted, and the entire quantity of rape-cake consumed during this period be taken into the calculation, we may assume that under otherwise not unfavourable circumstances 1 lb. of living weight is produced on an average from $2\frac{1}{2}$ lbs. of rape-cake, both with cattle and sheep; the quantity of nitrogen contained in the rape-cake and the increase of weight stands in a proportion of 0·129 to 0·036 lb., so that under such conditions nearly $\frac{3}{4}$ths, or at least $\frac{2}{3}$ds of the nitrogen originally present in the rape-cake becomes available in the dung, or in other words, the rape-cake loses only $\frac{1}{3}$rd of its value as a manure by its employment in fattening cattle.

From all the experiments and observations instituted, the author comes to the conclusion, that in flesh and milk formation, as in assisting to maintain the living weight of the animal, scarcely any food exercises a greater influence than rape-cake; and that in practical agriculture it is excelled by no other cattle food, when proper regard is paid to the quality of the manure produced by the cattle whilst being fed on it.—*Bericht über die Landwirthschaftl. Versuchsstation in Möckern*, 1853.

On the Action of Salts of the Protoxide of Iron on Pyroxyline. *By* A. Béchamp.

The author treated gun-cotton with protochloride of iron, and found that the filaments of the cotton became clothed with oxide of iron, whilst nitrous oxide gas was formed. The coating of oxide of iron was readily removed by muriatic acid. The analysis of the filaments, when thus cleaned, showed that they had regained the composition of cotton,—43·346 carbon, 6·309 hydrogen.

This cotton, treated by Braconnot's method for its conversion into sugar, furnished sugar, and a second substance, possessing the properties of dextrine.

When the author treated this substance with a mixture of 3 parts of fuming nitric acid and 5 parts of English sulphuric acid, it again became converted into pyroxyline, which exploded as violently as ever.

The author has thus restored the cotton from pyroxyline, and also, by changing the proportion of the protochloride of iron, starch from nitramidine (xyloidine), and gum from nitrated gum.—*Comptes Rendus*, xxxvii. p. 134.

1. *Action of Nitric Acid on the Chlorides of Potassium and Sodium.*
2. *Action of Oxalic Acid on the Nitrates and Chlorides of the same, with a ready method of converting them into the Carbonates.*

By Prof. J. Lawrence Smith, M.D.

This note is intended as an appendix to my researches for determining the alkalies in insoluble silicates in this Journal*.

During that investigation, many novel and interesting reactions were observed, several of which have already been alluded to. I present here one or two others of some interest.

1. It is well known that if nitric acid be added to a chloride, or hydrochloric acid to a nitrate, more or less of a decomposition will in either case ensue; but I believe it is not generally known how ready and complete the replacement is when nitric acid is heated with chloride of potassium or of sodium.

Among the experiments made, 40 grms. of nitric acid were boiled gently with 6 grms. of chloride of potassium, and in twenty minutes no trace of chlorine could be found in the liquid; the same is true when the chloride of sodium is used. The operations appear to depend on the oxidizing property of the nitric acid, with the liberation of chlorine that combines with some of the elements of nitric acid to form the chloronitric acid that readily passes off. The decomposition of the nitrates of the alkalies by hydrochloric acid does not readily take place, it not being complete even after repeated evaporations to dryness with a large excess of hydrochloric acid.

2. Before settling on the plan I now adopt, an easy method was sought for separating the alkalies from magnesia, by converting the two into carbonates, a plan that had previously been adopted; but the question with me was to change the nitrates to carbonates. The idea suggested itself of heating the nitrates with an excess of oxalic acid to the temperature at which the latter undergoes decomposition, when the nascent oxide of carbon might break up the constitution of the nitric acid, and the carbonic acid formed combine with the bases.

On making the experiment, I was surprised to see an abundant

* Chem. Gaz., vol. xi. pp. 252, 333.

evolution of nitrous acid vapours at a temperature considerably below 212°. It was clear that the oxalic acid decomposed the nitrate, liberating the nitric acid, which reacting on the excess of oxalic acid, gave rise to the nitrous acid vapours. If crystallized oxalic acid and the nitrate of potash or soda, the former in excess, be placed together in a flask, and heated over a water-bath, the mass soon enters into watery fusion; and at the temperature of from 130° to 140°, bubbles of gas are evolved, consisting of nitrous acid and carbonic acid. At 212° the evolution is vigorous; and if, after evaporation to dryness, the water be renewed several times, the nitric acid will be completely expelled from the nitre, there remaining the excess of oxalic acid and the oxalate of the alkalies.

It was natural to conclude from the above result, that oxalic acid would likewise decompose the chlorides of the alkalies, and on experiment the conclusion proved to be correct. If an excess of oxalic acid be mixed with either the chloride of potassium or of sodium, and the whole warmed gently, abundant vapours of hydrochloric acid are evolved; and by careful manipulation all the chlorine may be driven off under this form.

If heat be applied to the mass resulting from the action of oxalic acid on either the nitrates or the chlorides, all the oxalic acid will be expelled, and the oxalates converted into carbonates. A small amount of chloride of sodium can in this way be converted in a few moments into carbonate of soda, not however without some trace of the chloride being present. It is not my object to point to any special application of this decomposition; but it is one that may come into play in certain operations in analytical chemistry.

Experiments were made with the sulphate of the alkalies, to see if the oxalic acid had any decomposing action on them, expecting to test for free sulphuric acid by the action of the solution of the mass on zinc or iron, taking for granted that the presence of oxalic acid alone would not cause the evolution of hydrogen gas. Experiment however showed that this manner of testing the question was fallacious; and no other method suggesting itself, it was impossible to decide it positively. Sufficient was ascertained to show that if the sulphate was decomposed, it was only to a very minute extent.

In connexion with this last experiment, it is proved that zinc decomposes water readily in presence of oxalic acid, hydrogen gas being evolved; the action ceases in a short time, from the formation of insoluble oxalate of zinc; with iron, the action is very feeble, even when the solution is heated.

The decomposing action of oxalic acid on the nitrates and chlorides of alkalies appears to be due simply to the fact of a more stable acid being able to replace a more volatile one, and in no way measures the relative strengths of the acids; it being a well-established fact, that the physical as well as chemical properties of acids have much to do with their capability of replacing each other, a mere change of circumstances often reversing their relative action. —Silliman's *Journal*, November 1853.

On the Quantity of Ammonia contained in Rain-water, collected at a distance from Towns. *By* M. Boussingault.

The results obtained by the author, by observations made principally during the months of June and July last, appear to show that the rain which falls in the country contains considerably less ammonia than rain collected in a town. In seventeen observations, made between the 26th of May and the 5th of August, none of the water examined contained nearly 1 milligrm. of ammonia to the litre. The quantity contained in water collected at the Observatory in Paris varied from 1·08 milligrm. to 5·45 milligrms., the average being 3·35 milligrms. per litre.

The reality of this difference is confirmed by the circumstance, that four of the seventeen observations above mentioned coincide in point of date with experiments made at the Imperial Conservatory of Arts and Manufactures by M. Houzeau, viz. those of the 27th of May, the 19th–25th of July, of the 25th of July, and of the 28th–30th of July.

The water examined was collected at the ancient monastery of Liebfrauenberg, on the eastern slopes of the chain of the Vosges, and on the borders of the forests which extend into Bavaria.

		Ammonia in 1 litre of water. milligrm.
May	27. Continued rain	0·31
	27. At Paris	1·70
	28. Rain	0·51
	29. Violent rain	0·35
	30–31. Continued rain	0·25
June	2. Continued rain	0·25
	5. Uninterrupted rain for twenty-four hours	0·49
	21–24. Continued rain	0·61
	30. Rain and stormy rain	0·43
July	1–2. Continued rain	0·58
	13. Rain which fell between 9 and 10 o'clock at night, in a violent storm	0·68
	16. Rain which fell at 9 o'clock in the evening, during a storm; it was impossible to prove the presence of ammonia	0·00
	25. An extremely violent storm at 1 P.M.; much hail fell on the plain; at Liebfrauenberg the rain fell in torrents, but without hailstones	0·45
	25. Abundant rain for a short period at 9·30 P.M.	0·06
	19–25. At Paris	1·82
	25. At Paris	1·56
	28. At 6 o'clock in the morning	0·69
	29. At 4 o'clock in the morning, during a storm	0·15
	28–30. At Paris	2·00
Aug.	5. Rain at 8 o'clock in the morning	2·48

The following results, furnished by the examination of the water of the rivers of the valley of the Rhine, approach very closely to those given in the former part of the author's memoir:—

	Ammonia in 1 litre of water. milligrm.
Water of the Rhine, taken near Lauterbourg, in June..	0·49
Water of the Rhine, taken near the same place, in August	0·43
Water of the Moder, taken at Hagenau, in June.....	0·20
Water of the Seltz, taken at Merkwiller	0·13
Water of the Saüer, employed in irrigation	0·13
Water of the source of the Seltzbach	0·03
Water of the spring of the Liebfrauenberg	0·03
Water of the Lauter, taken at Wissenbourg, in July ..	0·31
Water of the Lauter, taken at Lauterbourg, in August	0·37
Well-water, from a farm near Haguenau	3·45

Comptes Rendus, August 8, 1853, p. 207.

Note on the Regeneration of Hippuric Acid. By M. Dessaignes.

The author caused chloride of benzoyle to react upon the zinc compound of glycocoll ($C^4 H^{10} N^2 O^4, ZnO$) in two manners,—

1. By heating the mixture to 248° F. in a closed tube.
2. By allowing the reaction to take place slowly in a flask closed with a ground stopper.

In both these operations hippuric acid was produced, and although in very small quantity, it was readily isolated, purified and recognized. The form of its crystals, the characteristic odour which it evolves, and the coal which it leaves, when burnt on platina foil, and the abundant production of ammonia observed when it is heated with potash, clearly distinguish it from benzoic acid. The quantity was not sufficient for analysis; but a small quantity of the silver salt was prepared, presenting the same crystalline form and the same solubility in water as hippurate of silver obtained from natural hippuric acid. This salt, dried at 212° F., was calcined, and left a residue of 38 per cent. of silver. Calculation requires 37·75, whilst the benzoate contains 47·16 per cent. of silver. There can consequently be no doubt of the regeneration of hippuric acid. The reaction may be expressed by the following equation:—

$$\left.\begin{matrix} C^4\ H^{10} N^2 O^4, ZnO \\ C^{14} H^{10} O^2, Cl^2 \end{matrix}\right\} = C^{18} H^{18} N^2 O^6 + Cl^2 Zn + H^2 O.$$

The author had tried chloride of benzoyle and glycocoll alone, but without success. There is either no action at all, or the action is too violent, according to circumstances; and the muriatic aci set free may be an obstacle to the combination.

Hippuric acid may be considered as a secondary acid, presenting

the constitution of the benzoïlsalicylamide of MM. Gerhardt and Chiozza, as shown by the comparison of the two following formulæ:—

$$N^2 \left\{ \begin{matrix} C^{14}\ H^{10}\ O^4 \\ C^{14}\ H^{10}\ O^2 \\ H^2 \end{matrix} \right\}, \qquad N^2 \left\{ \begin{matrix} C^4\ H^6\ O^4 \\ C^{14}\ H^{10}\ O^2 \\ H^2 \end{matrix} \right\}.$$

Benzoïlsalicylamide. Hippuric acid.

Comptes Rendus, August 8, 1853, p. 251.

On the Preparation of Hydroferrocyanic Acid. *By* Prof. Liebig.

When a cold saturated solution of ferrocyanide of potassium is mixed in small quantities with its volume of fuming muriatic acid, a snow-white precipitate, free from potash, of pure hydroferrocyanic acid is produced, if the muriatic acid be quite free from iron. It may be washed with muriatic acid almost without loss. When dried on a piece of tile, it dissolves readily and completely in alcohol, from which it may be obtained in beautiful crystals, free from muriatic acid, by solution in æther, and allowing the solution to separate into layers by standing.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 127.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

New Process for determining the Commercial Value of Animal Charcoal. *By* M. Corenwinder.

At present, when it is desired to determine the value of animal charcoal, it is usual to ascertain the amount of decolorizing power as compared with that of a charcoal, of which the properties are known, placing it as far as possible in the same physical condition as that which serves for comparison.

The decolorizing power of the charcoal ought undoubtedly to be taken into consideration; but this substance possesses another property, to which no serious attention has been paid, namely, an absorbent power.

In the present state of the sugar manufacture, the latter is certainly of more consequence than the decolorizing power, since, by means of centrifugal apparatus, the crystals of sugar may be completely freed from the coloured syrup which adheres to them. Moreover, the absorbent power of the charcoal produces the same effect as the decolorizing power, which is evidently due to the absorption of the coloured matters in solution in the syrup.

The comparative value of animal charcoal may consequently be determined from the quantity of lime which is absorbed by a given weight of that substance. This quantity, which is considerable with new charcoal, is much less with charcoal that has been revived; a

process may therefore be founded upon this property, which will serve to give a determinate value to animal black; and this so much the more because this very property is undoubtedly the one most important to the manufacturer, since it frees the syrups of a substance which is hurtful in the baking, and which prevents the crystallization of a certain quantity of saccharine matter.

This settled, it is easy to find a method by which every one may determine the value of animal charcoal. A solution of saccharate of lime is prepared; the number of degrees of the solution of sulphuric acid employed in alkalimetric analyses required to saturate a given volume (say 50 cub. centims.) of this saccharate is then determined.

This done, the samples of animal charcoal are reduced as nearly as possible to the same degree of fineness; equal quantities (say 50 grms.) of the samples are then put into separate flasks, and an equal quantity (say 1 decilitre) of the saccharate added to each, and left in contact for about an hour. The liquids are then filtered separately; and the quantity of the normal solution of sulphuric acid required to complete the saturation of 50 cub. centims. of each of them determined; the difference will show the quantity of lime which has been absorbed by each sample of animal black. That which absorbs the most is undoubtedly the best for the consumer, and that to which he should give the preference.

The saccharate of lime and the solution of sulphuric acid may be prepared in the following manner:—

An acid liquid is first prepared, composed of 20 grms. of pure monohydrated sulphuric acid diluted with water to exactly 1 litre.

A solution of saccharate of lime* is then prepared, of such a nature that it will be exactly saturated by the same volume of the dilute sulphuric acid. By adding the latter to 50 cub. centims. of the liquid filtered from the animal charcoal, it is easy to see how many degrees of the burette are required to complete the saturation of the lime. If 35 are required for this purpose, 100—35, or 65, represents the proportion of lime absorbed by the charcoal; this is therefore the number representing its standard. By operating with a burette graduated from the bottom, the degree of the charcoal experimented on may be read directly.

The author adds, that if these numbers be depended upon for the calculation of the absolute lime-absorbing power of the charcoal, they will lead to error, as it appears that this substance absorbs a

* If any given weight of lime would dissolve in a saccharine solution, it would require 11·40 grms. of pure lime to saturate 20 grms. of pure sulphuric acid; but as this is not the case, it is necessary to operate in the following manner:—

From 125 to 130 grms. of white sugar are dissolved in water, and 15 to 20 grms. of quick-lime added thereto; the liquid is then boiled, and filtered to separate the undissolved lime. It is then necessary to ascertain how many degrees of the normal acid are required to saturate 50 cub. centims. of this solution; if it takes 125, we get the following proportion:—125 : 100 :: 100 : $x = 80$. Consequently by taking 80 centilitres of the prepared saccharate, and diluting them with water to the volume of 1 litre, a solution of saccharate of lime is obtained, which saturates exactly its volume of the normal acid solution.

larger quantity of lime in proportion as the quantity in the solution is larger. An equilibrium is set up between the action of the charcoal, the dissolving force of the water, and the capacity of saturation of the sugar, which varies according to the quantity of these elements in the solution.—*Comptes Rendus*, Oct. 17, 1853, p. 610.

PATENT.

Patent granted to J. Napier, *for Improvements in separating certain Metals from their Ores and Alloys.*

This invention relates to the treatment of the ores and alloys of copper and tin.

In treating the ores of copper, the patentee proceeds in the following manner:—All those ores which contain sulphur, commonly termed sulphurets, are arranged in two classes, viz. those known or found by testing to contain tin as an impurity, and those that contain no tin. In dealing with ores of the first class, he mixes them, as far as practicable, in such proportions that the whole copper in the mixture shall range from 8 to 14 per cent. of the total weight of the ores. This mixture he then calcines in the ordinary way (well known to copper-smelters) until the quantity of sulphur remaining in the ore does not exceed a fifth of the weight of the copper, which may be ascertained by taking out a small sample, grinding it, and boiling 25 grs. in aqua regia for fifteen minutes, diluting the product with distilled water, filtering, and adding to the filtered liquor chloride of barium to precipitate the sulphur. This precipitate being collected, dried and weighed, contains 3 grs. of sulphur in every 22 grs. of its weight. But in the treatment of ordinary sulphuret ores, a period of calcination of from sixteen to eighteen hours is found to be sufficient to expel the excess of sulphur. The ore is then withdrawn from the calciner, and transferred to an ordinary fusing furnace; and to every ton of calcined ore about 1 cwt. of coal is added. This addition of coal is not essential to the process, but it is preferred to use it in order to obtain clean slag. The whole is then well fused, and the slagged matter being skimmed off in the usual manner, the "mat" or metallic portion is run off into sand-beds. At the bottom of the first and second beds is found a coarse alloy, known as "white metal," which consists mainly of copper, tin and iron, with small portions of such other metals as may have been contained in the ores. This white metal or alloy is removed and reserved for another process of treatment, to be hereinafter described; and the remainder of the mat (called "regulus" or "coarse metal"), now freed from the tin which was associated with the copper in the ores, may be roasted and refined by the ordinary methods; but it is preferred to calcine it again for eighteen hours, and then to fuse it along with other ores

containing no sulphur, such as those commonly imported from Australia, using equal weights of the ore and of the calcined regulus. A small proportion of coal should be added to this mixture to obtain clean slag. The product of this fusion, after a few hours' roasting in the usual manner, is fit for refining.

The second class of sulphuret ores (which contain no tin) is mixed in the same manner as the first class, but in such proportions that the copper in the entire mass shall not be less than 9 per cent. of the total weight; and this mixture is calcined for twelve hours, and fused in the manner above described. Should the copper in the ore have exceeded 12 per cent. of the total weight, it is preferred to add about 1 cwt. of coal to each charge, to prevent loss of copper in the slag. The coarse metal or regulus obtained by this fusion is calcined again for twenty-four hours, after having been ground or granulated in the usual manner. It is then fused with ores containing no sulphur, or with the calcined mat obtained by treating ores of the first class (containing tin), and the product obtained is treated by fusing, roasting and refining, according to the ordinary methods known and practised by smelters.

When the ores of copper contain tin and no sulphur, they are mixed with sulphuret ores, and in preference with such as contain tin, using such quantity of each kind as shall give the relative quantity of sulphur to the copper contained in the mixture in the proportion hereinbefore mentioned; and then the operation is proceeded with, in the manner above stated, by calcination and fusion, to obtain the metallic products, viz. regulus and white metal. When the earthy matters of the mixed ores are difficult to fuse, a little fluor spar, lime, or oxide of iron may be added as a flux; but in that case it is preferred to let the sulphuret ores be calcined for nine hours, or thereabouts, before mixing them with the other ores: the mass becomes, by this mode of treatment, easily fusible without flux.

The second part of this invention consists in a method of separating the tin and copper of the alloy known as white metal, whether produced by the process, or in the manner hereinbefore described, or by any other process whatever. The alloy is first ground to a fine powder by any of the ordinary processes, and the powder is then oxidized by subjecting it for a few hours to the common operation of calcining at a low red heat. When oxidized, the powder is black, and gives little nitrous fumes when a little of it is put into dilute nitric acid. But it may be oxidized also by direct chemical agency, as by heating it along with nitrates or other compounds which yield oxygen readily by heat.

When the powder has been completely oxidized, it is transferred to an iron pot containing caustic soda, in the proportion of not less than 1 lb. of dry caustic alkali to each pound of tin in the alloy. Heat is then applied to the pot (the materials being meantime stirred together) until the temperature is between 600° and 900° F., when the soda and oxide of tin combine, and form stannate of soda.

When the temperature has been maintained at a low red heat for about an hour, the mass is transferred from the pot to another vessel, and allowed to cool, and the pot is again charged with a new portion of soda and powder.

Caustic potash may be used instead of caustic soda; but in that case 30 lbs. of the dry alkali must be added for every 100 lbs. of the powder. Carbonate of soda or potash may also be used, but caustic soda is preferred. Instead however of oxidizing the powder in any of these ways, the oxidation may be effected by adding 30 lbs. of the nitrate of soda with 20 lbs. of caustic soda to 100 lbs. of the ground alloy in an iron pot (adding the alloy in small quantities at a time), and heating the mixture as above described. The metals are thereby oxidized, and the tin is dissolved. But additional care is necessary in this process, as the action of the nitrate salt on the metal is sudden and violent. When the melted mass, drawn from the pot, is cooled, water is added, which dissolves the stannate, and the oxides of copper and iron remain insoluble, and are separated by subsidence or by filtration. These oxides are removed, and mixed with the charge in process of roasting, by which the operation is facilitated and the metal is obtained. To the solution of stannate of soda, slacked lime, reduced to a pulpy state by water, is added (using about 27 lbs. of lime to every 100 lbs. of the stannate in solution), and boiled. During the boiling a little of the mixture is taken out every few minutes, and tested with lime-water until no precipitate is produced, when the process is complete. During this operation an insoluble stannate of lime is formed, which, when the boiling ceases, subsides to the bottom; and the caustic soda remaining in solution is used over again for dissolving the oxide from the powder. The stannate of lime is collected and dried; and to every 6 parts are added 2 parts of silica or sand, as free as possible from iron, and 1 part of anthracite coal or other carbonaceous matter, and the whole is fused in a reverberatory furnace, whereby the tin is obtained in the metallic state.

In extracting tin from its ores, the following mode is adopted:—The ores, after being washed and assorted, as now done, are, when constituting a sulphuret of tin, subjected to a short calcination, to convert the tin into an oxide; when however the ore is primarily an oxide of tin, no calcination is required. The ore is then treated in the manner before described with reference to calcined or oxidized alloy, about 7 lbs. of soda being used for every 10 per cent. of tin contained in the ore. All the operations afterwards necessary for obtaining the tin are the same as have been already described; but should the tin ore contain a little copper, which is often the case, then the copper will be left with the other insoluble matters in the ore when the stannate of soda is dissolved out, and may either be reduced by fusing with carbonaceous matters, or it may be collected, dried, and sold as copper ore.—Sealed April 23, 1853.

THE CHEMICAL GAZETTE.

No. CCLXX.—January 16, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Rape-oil, and two Acids prepared from it.
By Dr. F. Websky.

The author first shows it to be probable, that the statement that rape-oil contains margarine and oleine only rests upon supposition. Braconnot separated from it a white solid fat, which has since been taken for a mixture of these substances.

For his investigations the author had the oil pressed from good clean seed. The upper strata of such oil are greenish-yellow, the lower ones golden-yellow; it has a peculiar odour, which becomes stronger when the oil is heated; at 398° F. the oil becomes greenish-yellow. It dissolves in alcohol with difficulty, but readily in æther. At a temperature of about 662° F. the oil begins to decompose whilst boiling; combustible gases, which irritate the eyes, are evolved; and these condense into a fluid yellowish-green oil, of a strong odour and an acid reaction. If the oil be allowed to stand for six or eight hours in a narrow glass in ice, so that it may attain a temperature of 32° F., it congeals, acquiring the consistence of butter in summer. On solidifying, the temperature of the oil always rises several degrees.

The oil is nearly as slow in recovering its fluid condition as in becoming congealed; before it melts it attains a temperature of 41° or 43° F. Sulphur and nitrogen were not discovered in the oil. The greenish-yellow colouring matter of the oil appears to be soluble in water; it forms an insoluble compound with oxide of lead.

In investigating the acids of this oil, the author saponified it with oxide of lead and with soda. The lead-soap was treated with æther, the soda-soap with absolute alcohol. In both cases the salt of a very fluid acid was dissolved, that of a less fluid acid remaining behind. The acids separated from these salts were always coloured.

The author decomposed the soda-soap of the oil with muriatic acid, dissolved the fatty acid in an equal volume of alcohol of spec. grav. 0·835, and cooled the solution in ice. At 41° F. the entire mass was filled with crystals, which were purified and analysed. The author names this solid acid

Brassic Acid.—It has the composition $C^{45}H^{42}O^{3}+HO$. It is white, tasteless and inodorous; it fuses at 89°–91° F.; its point of solidification is at the utmost 2° below this. It is insoluble in water, but soluble in every proportion in absolute alcohol, or in alcohol of spec. grav. 0·835 at any temperature above its point of fusion.

When the solution cools, the acid shoots out in fine long needles, grouped in a stellate form round a point, like the crystallization of wavelite. At a temperature of 45° F., 12 parts of alcohol hold 1 part of acid in solution. From æther, with which the fused acid mixes in any proportion, it separates on cooling in a tallow-like state; the æther however retains much more acid in solution than the alcohol.

In its fused state and in its alcoholic solution it reddens litmus-paper. When heated to 104° F. for an hour, it undergoes no change; but longer exposure to heat and a higher temperature produce changes in it. Heated for some hours to a few degrees above its melting-point, it becomes a little yellowish; its melting-point sinks two or three degrees, but it retains its power of crystallization. If however it be heated to 212° F., in two days it acquires a citron-yellow colour, whilst the weight increases a very little. In this manner it gradually loses its power of crystallization; solidifies very slowly, in a tallow-like form, at a temperature which varies between 80° and 86° F.; some flakes of it, in one case, only fused at 98° F. It then has a peculiar aromatic odour. If it be heated to the above temperature for some days more, it becomes brownish, and loses a little in weight; but when heated to 266° F., the phænomena are produced much more rapidly, and it loses considerably in weight. These changes are assisted by the oxygen of the air. Analysis:—

Carbon.....	78·25	45	= 3375·0	78·26
Hydrogen	12·56	43	537·5	12·46
Oxygen	9·19	4	400·0	9·28

The atomic weight, calculated from the lead salt, was 4211, 4235, 4313, 4483, 4554, 4702, that is to say, the acid had already become changed during the purification of the salt. The soda salt gave 4231.

β Brassic Acid, $C^{45}H^{42}O^3$, HO or $C^{45}H^{43}O^4$, is obtained by treating brassic acid with nitrous acid. The rape-oil may also be treated in the first place with nitrous acid, and this acid then obtained by saponification. When purified by recrystallization, it is white, inodorous and tasteless. It solidifies in fine compressed needles, arranged in a dendritic form. The entire mass is much more compact than brassic acid, and has a dull satiny lustre. Its melting-point is between 138° and 140° F.; its point of solidification between 136° and 138° F. When heated for a considerable time to a temperature of 248° F., it exhibits the same changes as brassic acid; it loses its power of crystallization, becomes brownish, and smells exactly like the changed brassic acid. Crystallized from alcohol, it becomes tallow-like, forming therewith a white, soft, homogeneous mass. Analysis:—

Carbon	77·89	45	78·26
Hydrogen	12·58	43	12·46
Oxygen	9·53	4	9·28

The analysis of the soda salt gave the atomic weight of this acid as 4312·5.

The fluid residue after the preparation of the preceding acids is not oleic acid. The acid acquires a brown colour in the air, and also possesses a rancid odour. If saponified rape-oil be extracted with a little cold absolute alcohol, and the acid of the soda salt dissolved in the alcohol be separated by muriatic acid, this acid only exhibits faint traces of crystallization at 32° F.; if nitrous acid be passed through it, it becomes solid, thus forming a modification similar to elaidic acid. This criterion, however, which has hitherto been frequently employed as a test of oleic acid, is not certain, as brassic acid presents the same phænomenon. The acid from the rape-oil furnished on distillation a fluid from which no sebacic acid could be extracted, the opposite character being so distinct in oleic acid. Rape-oil must consequently contain little or no oleic acid.—*Journ. für Prakt. Chem.*, lviii. p. 450.

On the Acids of Rape-oil. By G. Stædeler.

Stædeler remarks, with reference to the preceding memoir, that brassic acid is very probably identical with the erucic acid of Darby, the formula for which, given by that chemist, is $C^{44} H^{42} O^4$ *. He is also of opinion that the fluid acid may perhaps be identical with the fluid acid of oil of mustard, the baryta salt of which, according to Darby, is $BaO, C^{38} H^{36} O^4$. Stædeler thinks that the formula of this salt is perhaps $BaO, HO + C^{38} H^{35} O^3$, so that the uncombined acid may have the same composition as was found for the oil of the *Balœna rostrata* by Scharling†; it is not however identical with this. Moreover, Darby's analyses also agree with the formula $C^{40} H^{37} O^3 + 2HO$, and it is consequently possible that the formula of the acid of oil of mustard is $C^{40} H^{38} O^4 = HO, C^{40} H^{37} O^3$.

The author has already put together under the general formula $C^n H^{n-2} O^4$ a series of acids, which are distinguished from the acids of the series $C^n H^n O^4$ only by containing 2 equivs. of hydrogen less. Six acids have as yet been ranged in this series:—

$C^n H^{n-2} O^4$.	$C^n H^n O^4$.
$C^{44} H^{42} O^4$, erucic acid.	$C^{44} H^{44} O^4$, behenic acid.
$C^{38} H^{36} O^4$, Scharling's acid.	$C^{38} H^{38} O^4$
$C^{36} H^{34} O^4$, oleic acid.	$C^{36} H^{36} O^4$, stearic acid.
$C^{30} H^{28} O^4$, moringic acid.	$C^{30} H^{30} O^4$, cetic acid.
$C^{14} H^{12} O^4$, damaluric acid.	$C^{14} H^{14} O^4$, œnanthic acid.
$C^6 H^4 O^4$, acrylic acid.	$C^6 H^6 O^4$, propionic acid.

In the same series perhaps come the acid of the oil of mustard, $C^{40} H^{38} O^4$?, and also the oil separated by Heintz from the baryta salts of the acids of spermaceti, $C^{28} H^{26} O^4$?, and the damolic acid, $C^{26} H^{24} O^4$?. The property of being converted by the action of nitrous acid into isomeric crystalline acids probably occurs in all the members of the series $C^n H^{n-2} O^4$, and it is therefore not improbable that some other crystalline acids, the composition of which agrees with this formula, but which cannot be arranged in one series with oleic acid, must be arranged with elaidic acid; such are cam-

* Chem. Gaz., vol. vii. p. 163. † *Ib.*, vol. vii. p. 163.

pholic acid, $C^{20}H^{18}O^4$, and angelic acid, $C^{10}H^8O^4$.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 133.

On the Occurrence of Nickel and Cobalt in some mineral Springs, and on a Method for their Isolation. *By* Ossian Henry.

Mazade some time since stated that he had found in the chalybeate springs of Neyrac and its ochreous deposits, titanium, glucina, cobalt and nickel. In consequence of this statement, the author has tested several chalybeate waters for nickel and cobalt, and ascertained the presence of these two metals by the following process:—

To a large quantity of the water a slight excess of carbonate of soda is added; the fluid is then allowed to stand in the air until the iron is completely converted into oxide and deposited. The deposit of the spring itself may also be taken. These deposits are dissolved in muriatic acid, and evaporated to a certain degree for the removal of the glucina, titanium, sand and silica, when the solution generally contains only alumina, lime, magnesia, iron, manganese, nickel and cobalt.

To this solution carbonate of soda is again added until a precipitate is obtained, which is agitated in the air with a large quantity of water. It is then washed; and when it has become oxidized in the air, it is brought into contact with water which has been saturated with carbonic acid in an apparatus fitted for the purpose. This dissolves only the carbonates of nickel and cobalt, upon which sulphuretted hydrogen is passed through the solution, or hydrosulphuret of sodium added to it.

By this means the nickel and cobalt are separated, generally very slowly, in the form of sulphurets. The sulphurets are dissolved in nitromuriatic acid, precipitated by carbonate of soda, and treated in the manner proposed by Laugier for the detection of cobalt and nickel.—*Journ. de Pharm. et de Chim.*, 3rd ser. xxiv. p. 305.

On the Occurrence of Aldehyde amongst the Products of the Distillation of Sugar. *By* C. Völckel.

In my memoir upon the products of the distillation of sugar*, a volatile fluid is described under the name of "*yellowish fluid*;" it is the first that comes over during the distillation of sugar-vinegar, begins to boil at 86° F., and distils over for the most part between 140° and 149° F. Closer investigation showed that this fluid contained acetone, a volatile yellow-coloured oil, and very probably aldehyde. The latter betrayed itself by its characteristic odour, and its behaviour with solution of potash and nitrate of silver and ammonia. Wood-spirit could not be detected in this fluid.

In the above memoir I left it undecided whether aldehyde really does occur amongst the products of the distillation of wood, until I should have the opportunity of instituting some further experiments with this view. In fact, in my former investigation, the greater part

* Ann. der Chem. und Pharm., lxxxv. p. 59; Chem. Gaz., vol. xi. p. 461.

of the yellowish fluid was employed in the endeavour to ascertain whether or no wood-spirit occurred amongst the products of the distillation of sugar; the smaller portion, which was specially intended for the search for aldehyde, was lost in consequence of the application of too strong a heat in driving off the water, during an attempted separation of the acetone from the aldehyde by means of finely-powdered chloride of calcium. The positive proof of the existence of a very small quantity of aldehyde amongst the products of the distillation of sugar did not appear to me, at that time, when I was still much occupied with the investigation of the other products of the dry distillation of sugar and wood, of such importance that I should again undertake a series of distillations of sugar, especially as the formation of aldehyde during the decomposition of organic bodies had already been demonstrated by Hess and Scanlan. I have however since endeavoured to fill up this gap in my previous investigations.

During the distillation of sugar-vinegar, a yellow fluid, of penetrating aldehyde-like odour, is the first thing to pass over. This was rectified for further examination on the water-bath, with the addition of a small quantity of solution of carbonate of soda to neutralize any adherent acids; it was then deprived of water by chloride of calcium, and distilled, the matter first passing over being especially collected. This fluid has still a slight tinge of yellow. It mixes in all proportions with anhydrous æther. If this mixture be saturated with anhydrous ammoniacal gas, colourless crystals are produced in a short time, possessing all the properties of aldehyde-ammonia. Not the smallest doubt therefore can exist that aldehyde is formed during the distillation of sugar, although in very small quantity.

Aldehyde is also certainly present in small quantity in the products of the distillation of wood, and is perhaps the cause that wood-spirit, which has been freed by distillation upon lime from those oils, such as furfurole, which are volatilized with difficulty, and by these means rendered colourless, again acquires a colour, and deposits a brown substance when caustic potash is dissolved in it.

The occurrence of a small quantity of formic acid in sugar-vinegar is probably intimately connected with the formation of aldehydes during the distillation of sugar. Thus both together contain the same equivalents of hydrogen and oxygen :—

1 equiv. aldehyde ..... $= C^4 H^4 O^2$
1 equiv. hydrated formic acid $= C^2 H^2 O^4$
$C^6 H^6 O^6$

The simultaneous formation of aldehyde and formic acid by the exposure of sugar to heat may therefore be as readily understood as the formation of the hydrates of carbon, acetic acid, assamar and furfurole.

The yellow colour of the fluid passing over at 149° F., which both according to the previous and the present investigations consists essentially of acetone and aldehyde, arises from the presence

of yellow, volatile, readily-changeable oils, which distil over principally between 176° and 320° F., and possess a different constitution from furfurole.

These oils are produced only in very small quantity in the distillation of sugar. They possess a strong penetrating odour, and are converted into brown substances, which are only sparingly soluble in potash, by the action of alkalies, or even of their carbonates. The true constitution of these volatile oils could not be ascertained, as the small quantity in which they were obtained admitted of no further separation.

In my previous investigation, only that portion of them which passed over between 284° and 302° F., which however is always much contaminated with furfurole, whose boiling-point is 324° F., was submitted to analysis. In the present case, that portion of these volatile oils which distils between 176° and 212° F. was also analysed.

0·2085 grm. of this fluid gave 0·479 grm. of carbonic acid and 0·182 grm. of water. In 100 parts—

Carbon	62·72
Hydrogen	9·69
Oxygen	27·59

The whole quantity of this oily fluid, which was obtained from the products of distillation of 8 lbs. of sugar, amounted only to between 2 and 3 grms. The fluid is lighter than water, in which it is tolerably soluble, especially with the assistance of heat. It communicates a yellow colour to water.

This oily fluid is also present in the products of the distillation of wood; with furfurole it is the cause of the yellow colour of crude wood-spirit.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 303.

On the Occurrence of Malate of Lime in the Leaves of the Common Ash. By MM. GAROT.

The leaves of the ash have been recently employed in medicine. They are said to be efficacious in gout, and according to Emile Mouchon they are aperient. From the author's investigations, these leaves contain malate of lime. The simple infusion of the leaves is sufficient for the extraction of the lime salt, which is held in solution in this infusion by means of a gummy or extractive matter. From 1 kilogrm. of the leaves the authors obtained about 50 grms. of malate of lime, which was readily separated from the infusion when the latter was evaporated to the consistence of a syrup; when washed, it was perfectly white.

From this, the authors are of opinion that the leaves of the ash contain quite enough of this salt to give them a medicinal action.

They have separated the acid from the lime salt. It formed an acid syrup, soluble in water, with no signs of crystallizability. Semi-saturated with ammonia, it furnished the acid ammoniacal salt in crystals. It is from this circumstance that the authors conclude that the acid is malic acid, as they did not analyse it.—*Journ. de Pharm. et de Chim.*, 3rd ser. xxiv. p. 308.

On some new Sulphites of Copper.
By M. L. PÉAN DE ST. GILLES.

Simple sulphites of copper do not appear to exist.

The double sulphites may be referred to three distinct classes:—

1. *Sulphites of the Peroxide and Protoxide of Copper.*—These double salts are formed by the action of sulphurous acid, or of the alkaline sulphites on salts of the oxide of copper, employed in excess.

2. *Sulphites of the Protoxide of Copper and Alkalies.*—These are obtained by treating a salt of copper with an excess of alkaline sulphite.

3. *Intermediate Sulphites or Green Sulphites.*—These are true double salts, formed by the union, atom for atom, of sulphites of the first and second series:—

I. *Sulphites of the Peroxide and Protoxide of Copper.*

Yellow Sulphite (Cu^2O, SO^2), (CuO, SO^2), 5HO.—This salt is amorphous, of a slightly greenish-yellow colour, insoluble in water, but soluble without decomposition in sulphurous and acetic acids. It also dissolves in the salts of the oxide of copper, to which it communicates an emerald-green colour. Potash changes it into a greenish oxide, the colour of which is due to the mixture of the blue hydrate of the oxide, with the yellow hydrate of the protoxide; it undergoes no change in dry air, and dissolves in ammonia with a blue colour. Its analysis gave the following results:—

	Calculated.	Found.	
3Cu	43·17	43·42	43·31
$2SO^2$	29·09	29·16	28·70
5HO	20·45	20·16	

It is prepared in a perfectly pure state by slowly passing a current of sulphurous acid into a solution of acetate of copper. The salt is deposited in the form of a flocculent precipitate, which disappears completely on the addition of more acid. It is also produced by the mixture of an alkaline sulphite with a salt of the oxide of copper; but when thus prepared, it almost always contains a certain quantity of the alkaline sulphite.

Red Sulphite, (Cu^2O, SO^2), (CuO, SO^2) 2HO.—All solutions of the preceding salt, deposit, on evaporation, a red salt, which has been well described by M. Chevreul and analysed by M. Rammelsberg. It only differs from the yellow sulphite by the want of 3 equivs. of water, but its properties are completely distinct. The solvents of the preceding salt have no action upon it, and potash separates an oxide from it, which instead of green is brownish; it contains yellow protoxide of copper mixed with anhydrous oxide of copper, which is black.

The production of these sulphites may be explained in the following manner:—Whenever an alkaline sulphite is brought into contact with a salt of the oxide of copper, a reduction and a double exchange are simultaneously produced, which gives rise to the yellow sulphite of the oxide and protoxide of copper. Thus—

1. $$\left\{\begin{array}{l} 3(CuO, \overline{A}) + 4(KO, SO^2) + 5HO \\ = (Cu^2O, SO^2), (CuO, SO^2), 5HO + KO, SO^3 + 3KO, \overline{A} + SO^2. \end{array}\right.$$

When a haloid salt of copper has been employed, this reaction is still followed by a double exchange, determined by the insolubility and stability of the haloid salt of copper which is liable to be formed; thus—

2 $$\left\{\begin{array}{l} (Cu^2O, SO^2), (CuO, SO^2), 5HO + 2KCl \\ = Cu^2Cl + CuCl + 2KO, SO^2 + 5HO. \end{array}\right.$$

We then fall back upon the reaction 1, and the decompositions succeed one another alternately in this manner until the complete destruction of the alkaline sulphite.

But when, on the contrary, an oxysalt is acted upon, this double exchange is not produced, because simple oxysalts of the protoxide of copper do not exist. [I have been unable to obtain a single one in the humid way; the reaction of nitrate of silver with protochloride of copper, recommended by Berzelius, only gives rise to the formation of nitrate of copper, with deposition of metallic silver.] The sulphite of the oxide and protoxide of copper consequently remains, and this is verified by all the examples which I have indicated.

The action of free sulphurous acid must be assimilated in this respect to that of the alkaline sulphites. This action, which is always very distinct, has even furnished me with the application of an important principle, laid down by Berthollet in his 'Statique Chimique,' and verified quite recently by the ingenious experiments of M. Malaguti. Thus sulphurous acid, according to this principle, acts *in the ratio of its mass* upon the oxide of the sulphate, and produces a certain proportion of yellow sulphite of oxide and protoxide of copper, which remains dissolved by the excess of acid employed. By an elevation of temperature, this acid resumes its gaseous elasticity, and the sulphite then becomes dissolved in the sulphate of copper, to which it gives an emerald-green colour; then, lastly, it is decomposed by the sulphuric acid first eliminated, which dissolves the oxide of copper, and decomposes the protoxide, from which it separates the metallic copper in crystalline spangles.

II. *Sulphites of the Protoxide of Copper and Alkalies.*

The double sulphites produced by potash, and more especially by soda, are very changeable and difficult to obtain pure. I have prepared the two following double salts by treating the protochloride of copper with an excess of sulphite of ammonia:—

Sulphite A, $(Cu^2O, SO^2), 7(NH^3, HO, SO^2), 10HO$ (unknown).—This sulphite crystallizes in great abundance in fine needles, which redissolve with ease in their mother-liquor with the assistance of heat; on cooling, they are again deposited in voluminous prisms. Exposed to moist air, it rapidly absorbs oxygen and acquires a blue colour, diffusing an odour of ammonia.

Sulphite B, $(Cu^2O, SO^2), (NH^3, HO, SO^2)$, (M. Rogojski).—This salt is produced when the solution of the preceding salt is saturated with sulphurous acid. It is insoluble in water, and, like

the preceding, unalterable as long as it remains immersed in its mother-liquor. M. Rogojski states that he has prepared the simple red sulphite of the protoxide of copper by exhausting the action of the sulphurous acid upon this sulphite of ammonia and copper. I have assured myself that the reaction pointed out by this chemist only takes place in contact with the air, and that the product obtained in this case is the red sulphite of the oxide and protoxide of copper more or less free from the ammoniacal salt. The following expression will show clearly why sulphurous acid accelerates the oxidation of this salt under the influence of the air:—

$$3[(Cu^2O, SO^2), (NH^3, HO, SO^2)] + O + SO^2 + 2HO$$
$$= 2[(Cu^2O, SO^2), (CuO, SO^2)\,2HO] + 3(NH^3, HO, SO^2).$$

III. *Intermediate Sulphites.*

When two concentrated solutions of sulphite of ammonia and sulphate of copper are saturated with sulphurous acid and then mixed, the sulphite formed remains dissolved in the excess of acid, and the liquid only becomes green. At the end of some hours an abundant crystallization of a salt of a clear green colour is deposited; this does not redissolve in its mother-liquor. It is an intermediate sulphite, produced by the union, atom for atom, of the yellow sulphite with the sulphite B of copper and ammonia. It has therefore the following formula:—

$$[(Cu^2O, SO^2), (NH^3, HO, SO^2), (Cu^2O, SO^2), (CuO, SO^2), 5HO].$$

I have obtained a potash salt isomorphous with the preceding, and the composition of which corresponds exactly with that; but it is much more difficult to prepare, and changes more rapidly.

To resume, the essential characters of the sulphites of copper give reason to attribute to sulphurous acid an action precisely intermediate between that of the other oxyacids and that of the hydracids in the saline combinations of this metal. Thus whilst the oxyacids cannot in any form combine with the protoxide of copper in the humid way, and whilst the hydracids, on the other hand, furnish few very stable compounds with oxide of copper, sulphurous acid, although it certainly does not give any simple salt of copper, furnishes double salts of remarkable stability, which have for their principal type the combination of the two sulphites of the oxide and protoxide of copper.

At the close of this paper, M. Chevreul communicated the following facts relative to the history of the sulphites of copper:—

Fourcroy and Vauquelin made known the yellow precipitate obtained by the mixture of the solutions of an alkaline sulphite and of a salt of the protoxide of copper under the name of *sulphite of copper*. M. Chevreul showed that this precipitate was a double sulphite of protoxide of copper and alkali. By causing sulphurous acid to act upon the protoxide of copper, he obtained sulphate of copper and a red sulphite of the protoxide. He remarked that he had always found a little protoxide of copper in all the sulphites of copper that he had prepared.—*Comptes Rendus*, June 20, 1853, p. 1086.

On the Occurrence of Iodine. By C. Barreswil.

The author points out, that many, or even all the reagents employed for the detection of iodine, are frequently contaminated with that substance.

Nitric acid very commonly contains iodine. The iodine is very readily detected in this case, by diluting the acid with an equal volume of water, putting it into a retort furnished with a gas-tube, and passing the vapours into a test-tube containing very clear starch-paste.

Nitrates of potash and soda generally contain iodine. The salts to be examined are to be treated with nitric acid free of iodine, and tested as in the previous experiment. These two salts are treated in the same manner, to prepare nitric acid free from iodine from them. 5 parts of nitric acid are sufficient for 100 parts of nitrate of soda.

Sulphuric acid usually contains iodine, arising from the nitrate of potash with which the sulphur was burnt. The iodine is to be detected as in the preceding cases.

Muriatic acid contains iodine from its being prepared with sulphuric acid. It is therefore necessary, in testing for iodine, before all things to employ reagents perfectly free from iodine. For this purpose potash must be prepared from nitrate of potash, obtained pure by repeated recrystallization. From this, sulphate of potash is formed, and this readily furnishes potash free from iodine by precipitation with pure baryta.

In examining bromine for iodine, the bromine is to be poured into a solution of sulphate of iron in great excess; the bromine disappears very rapidly. Nitric acid, free of iodine, is now to be added until the fluid becomes dark brown, when it is to be heated, as in the testing of nitric acid for iodine.

In conclusion, the author remarks that he publishes this notice as preliminary to a memoir in which he proposes to show that iodine has been found in many substances in which it does not exist.—*Journ. de Pharm. et de Chim.*. 3rd ser. xxiv. p. 346.

Upon Æsculine. By F. Rochleder *and* R. Schwarz.

The authors have continued their investigation of æsculine, by treating this substance with emulsine; they have obtained the following results:—

When æsculine is dissolved in cold water, and the saturated solution mixed with a solution of emulsine (from sweet almonds), and exposed to a temperature of 79°–86° F., a turbidity is soon produced in the fluid, and a layer of a white powdery body is gradually deposited on the bottom of the vessel. The fluid loses the bitter taste which it originally possessed, and at last acquires a sweet taste; the substance deposited on the bottom of the vessel is æsculetine, as was shown by its properties and composition after recrystallization from boiling water. A small portion of this substance is dissolved in the fluid.

If the fluid be evaporated in the water-bath, and the residue treated with hot alcohol, the emulsine remains undissolved, whilst

æsculetine and sugar are dissolved. These two substances are separated by treatment with cold water, in which æsculetine is difficult of solution; or more completely by the precipitation of the boiling solution with sugar of lead, filtering the fluid from the compound of æsculetine and oxide of lead, removal of the lead by sulphuretted hydrogen, and evaporation of the fluid separated from the sulphuret of lead to the consistence of syrup. The sugar thus obtained ferments on the addition of yeast, and reduces alkaline solution of oxide of copper to protoxide. The analysis of the sugar, dried at 212° F., gave the following result:—

Carbon	40·50	12 =	72	40·00
Hydrogen	7·38	12	12	6·66
Oxygen	52·12	12	96	53·34

The authors endeavoured to determine the quantity of sugar formed from a certain quantity of æsculine in this manner, and found that 1·032 grm. of æsculine furnished 0·7300 grm. of grape-sugar dried at 212° F. In accordance with the admitted formula of æsculine, 0·7676 grm. of sugar should have been obtained, which comes as near the result of the experiment as can be expected in investigations of this kind. The composition and constitution of æsculine, as well as its decomposition by emulsine and dilute mineral acids, will consequently be well represented by the following equations:—

$C^{42} H^{24} O^{26}$ æsculine $= 2(C^{12} H^{10} O^{10}) + C^{18} H^{4} O^{6}$ anhydrous æsculetine.

$C^{42} H^{24} O^{26}$ æsculine $+ 6HO = 2C^{12} H^{12} O^{12} + C^{18} H^{6} O^{8}$ æsculetine.

Sitzungsb. der Akad. der Wiss. zu Wien., 1853, p. 334.

On the Influence of Pressure upon the Formation of Chemical Compounds. *By* Prof. Wöhler.

Hydrate of chlorine, which is immediately decomposed at ordinary temperatures and at the pressure of the atmosphere, remains for the most part undecomposed even at a summer heat when enclosed in hermetically-sealed tubes, under the pressure of the chlorine which is set free from a portion of it which undergoes decomposition. In such a tube, when plunged into water of a temperature of 86°–104° F., the hydrate of chlorine is decomposed, but becomes partially restored on its return to the ordinary temperature.

This decomposition is not prevented by the exclusion of the air under the pressure of chlorine gas of the tension of the atmosphere; under these circumstances the decomposition takes place as usual at any temperature above 32° F.

A tube in which hydrate of chlorine was hermetically sealed was exposed to the sun for a whole summer's day. It became fluid, but did not indicate decomposition of the water by the setting free of oxygen.

The author had already observed, that during the preparation of liquid sulphuretted hydrogen from sulphuret of hydrogen in hermetically-sealed tubes, colourless crystals are sometimes formed, which immediately disappear on the tube being opened.

In two tubes, in which sulphur, but no liquid sulphuretted hydrogen had separated, these crystals were found in large quantity; they did not however make their appearance in a third tube, in which the persulphuret of hydrogen was enclosed together with concentrated muriatic acid. Hence the author concludes, that the crystalline compound, which is no doubt a hydrate of sulphuretted hydrogen, must be produced when a small quantity of water is enclosed with hydrate free from acid; the water then combines with the sulphuretted hydrogen under the pressure of the condensing sulphuretted hydrogen (17 atmospheres). Under this pressure it is permanent at ordinary temperatures. If the tube be heated in water to 86° F., the compound dissolves, and rapidly becomes fluid, returning to a solid state again on being cooled to the ordinary temperature.—*Ann. der Chem. und Pharm.*, lxxxv. p. 374.

Researches on the Æthers. *By* M. Berthelot.

I. *Formation of the Compound Æthers by means of Æther and Acids.*

Can æther, formed at the expense of alcohol by elimination of water, reproduce the alcohol whence it has arisen, or at least the combinations of which this alcohol forms an integral part? This question has been proposed more than once; and in spite of certain facts repeatedly announced, it is not, I think, regarded as settled. Nevertheless it is not perhaps without some importance. In fact, in a theory widely received, the compound æthers are represented by an anhydrous acid combined with oxide of æthyle, a substance isomerous or identical with æther. The direct production of the compound æthers by means of æther and the acids has a tendency to support this view, although it is also susceptible of other explanations.

This production is effected by heating the acid and æther, enclosed in very strong tubes, to about 680°–752° F.

The author has procured benzoic æther in this manner from æther and benzoic acid. It possessed the odour and specific properties of benzoic æther, boiled at 416° F., and gave on analysis—

		Formula.
Carbon	72·2	72·0
Hydrogen	6·7	6·7

Treated with potash and water, it reproduces the benzoic acid; and in place of the æther, a volatile inflammable liquid, soluble in water, which, when touched with a drop of a mixture of sulphuric and butyric acids, evolves the odour of butyric æther. These characters belong to alcohol.

The æther employed in the preceding experiment had been shaken five times with its volume of water, so as gradually to dissolve the half; it was then dried upon chloride of calcium, and rectified. After nine hours' contact with the benzoic acid at 680° F., it furnished 30 per cent. of benzoic æther (16 grms. produced 5 grms.). The formation of the benzoic æther commenced at 572° F.; but at this temperature, even after long contact, there was but little of it.

With the view of acquiring greater certainty with regard to the purity of the æther employed, the author rectified the æther purified by the above method, distilling only the half of it at a fixed temperature; the distillation was then repeated upon this portion, only collecting the half of the product. The æther thus obtained furnished 25 per cent. of benzoic æther after three hours' contact with the acid at 680° F.

Æther and butyric acid, kept for six hours at 680° F., produced butyric æther. The liquid in the tubes, submitted to distillation, only furnished æther, water, butyric æther and butyric acid. No gas was evolved.

At the same temperature, æther and palmitic acid produced palmitic æther, fusible at 72° F.

In these instances neither the acid nor the æther was entirely combined, whatever might be the excess of one or other of them.

Æther and water, heated to the limit of decomposition (842° F.?), do not combine.

II. *Direct Formation of the Æthers by means of Alcohol and Acids.*

The union of acid and alcohol to form æther is effected either directly or by the intervention of a mineral acid. The direct combination is generally easy with the energetic acids; but with the organic acids, such as acetic acid, becomes very slow and incomplete. But with the aid of sulphuric acid, the combination is immediately and almost completely effected.

The author has arrived at the following results by employing close vessels, and the assistance of long exposure to heat, in the direct preparation of the æthers:—

At 392°–482° F., the combination of the alcohols with the fatty acids is effected with rapidity. In this manner the author produced at 482° F. the following æthers:—

Methylopalmitic æther, a crystalline substance, fusible at 82° F., solidifying at 72° F.;

Æthylopalmitic æther, fusible at 70°·7 F., solidifying at 64°·4 F., and reproducing, by the action of potash, palmitic acid, fusible at 142° F.; and

Amylopalmitic æther, a waxy substance, fusible at 48° F.; with potash it reproduces palmitic acid, fusible at 142° F.

The combination of the alcohols with the fatty acids is never complete, either for the alcohol or the acid. But these three æthers are most abundantly formed in the presence of an excess of acid, which is afterwards separated by lime and æther. When heated afresh to 500° F. for fourteen hours with eight or ten times their weight of palmitic acid, they are found after the operation to have undergone no change whatever.

With thirty hours' contact at 212° F., benzoic, acetic, and butyric æthers were produced in great abundance, especially the latter. Stearic æther even begins to be formed in 102 hours, but in very small quantity. The addition of acetic acid to the mixture in the latter case causes the stearic acid to become completely ætherified in 102 hours. This corresponds with the known action of sulphuric

and muriatic acids, only differing in the comparative weakness of the acetic acid. It appears especially in this case, that the combination of the stearic acid with the alcohol is induced by that which takes place between the acetic acid and the same alcohol. It is a pretty clear instance of the propagation of molecular movement.

The ready ætherification of the fatty acids in an alcoholic liquid, rendered acid even by acetic acid, appears to the author often to render the purification of these bodies very delicate.

III. *On the Decomposition of the Æthers.*

The æthers are split by the same agents which cause their formation. Thus—

Water heated to 212° F., for 102 hours, with stearic and oleic æthers, begins to split them, with regeneration of stearic and oleic acids. Under these conditions it does not act at all upon benzoic æther.

Acetic acid, diluted with 2 or 3 vols. of water, when in contact with stearic æther for 106 hours at 212° F., distinctly acidifies the stearic æther without producing acetic æther; it partially decomposes butyric and benzoic æthers, with formation of butyric and benzoic acids.

Fuming muriatic acid, in 106 hours, at 212° F., produces double decomposition with acetic, butyric, benzoic and stearic æthers. The acids are set free, and muriatic æther is formed. The decomposition is never complete, unless in the case of stearic æther.

Thus a weak acid may be ætherified or its æther decomposed at will under the influence of muriatic, or even of acetic acid. This difference in the action of the same substance results from the presence of an excess of water in the one case, of alcohol in the other. The mass and relative energy of the acids are also to be taken into account.—*Comptes Rendus*, Dec. 5, 1853, p. 855.

PROCEEDINGS OF SOCIETIES.

Royal Society.

December 8th, 1853. (Colonel Edward Sabine, R.A., V.P. and Treasurer, in the Chair.)

"On some of the Products of the decomposition of Nitrotoluylic Acid." By Henry M. Noad, Ph.D., Lecturer on Chemistry at St. George's Hospital.

The author refers to a former memoir in which he described the mode of preparation and properties of two new organic acids, the analogues of benzoic and nitrobenzoic acids in the toluyl or immediately succeeding series, and to which the names of toluylic ($C^{16}\ H_8\ O_4$) and nitrotoluylic ($C_{16}\ H_7\ (NO_4)\ O_4$) acids were consequently given.

In the present paper he resumes the study of the action of nitric acid on cymol ($C_{20}\ H_{14}$), and describes first some unsuccessful attempts to procure from that oil the substitution compound $C_{20}\left\{\begin{matrix}H_{13}\\NO_4\end{matrix}\right\}$, from which, by the action of reducing agents, he had

hoped to procure a new organic base homologous with aniline, toluidine, &c. He then investigates the products of the decomposition of his new nitrogen acid. He describes the preparation and properties of nitrotoluylamide $C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4$, NH_2, and having succeeded, though by a rather tedious process, in obtaining this substance in some quantity, he studies the action of reducing agents on it. By the action of hydrosulphate of ammonia upon an aqueous solution of the amide, a crystalline substance was procured, which analysis proved to be homologous with the *carbamide—carbanilide* of Hofmann, and with the *anilo-urea* of Chancel. The study of its properties showed that it must be considered as the analogue of the latter, that it is the true urea of the toluyl series, being a well-defined organic base, forming a series of crystalline salts, of which the nitrate and oxalate were qualitatively examined. A synoptical view of these ureas is given, showing their relation with the urea type.

By the action of a boiling solution of caustic potash on toluyl urea ($C_2 H_3 (C_{14} H_7) N_2 O_2$), a new acid was procured, the analysis of which showed that it has three homologues in the benzoyl series, viz. *anthranilic acid, benzamic acid,* and *carbanilic acid,* all of which are represented by the formula $C_{14} H_7 NO_4$, the composition of the new acid being expressed by the formula ($C_{16} H_9 NO_4$).

The limited quantity of this acid at the author's disposal, and the great difficulty with which it was procured, did not enable him to decide positively with which of the above acids it corresponds, though its mode of formation would render it probable that it is the true analogue of *carbanilic acid.* The determination of this question is of some interest, inasmuch as should it prove to correspond to *anthranilic acid,* a road might through it be opened for the introduction of a series of new substances at present entirely wanting, namely, the proper homologues of *salicylic* acid and its derivatives. The author proposes to return to this subject, and he gives, in conclusion, a synoptical view of those corresponding members of the *benzoyl* and *toluyl* groups which in the present and former paper he has established.

Dec. 15, 1853. (Thomas Bell, Esq., V.P., in the Chair.)

"On the Acidity, Sweetness, and Strength of Wine, Beer and Spirits." By H. Bence Jones, M.D., F.R.S.

(1.) The acidity of the different liquids was determined by means of a standard solution of caustic soda. The quantity of liquid neutralized was always equal in bulk to 1000 grs. of water at 60° F.

The acidity in different—

Sherries	varied from	1·95	grs. to	2·85	grs. of caustic soda.
Madeira	,,	2·70	,,	3·60	,,
Port	,,	2·10	,,	2·55	,,
Claret	,,	2·55	,,	3·45	,,
Burgundy	,,	2·55	,,	4·05	,,
Champagne	,,	2·40	,,	3·15	,,
Rhine wine	,,	3·15	,,	3·60	,,
Moselle	,,	2·85	,,	4·50	,,

Brandy	varied from	0·15	grs. to	0·60	grs. of caustic soda.
Rum	,,	0·15	,,	0·30	,,
Geneva	,,	0·07			,,
Whisky	,,	0·07			,,
Bitter ale	,,	0·90	,,	1·65	,,
Porter	,,	1·80	,,	2·10	,,
Stout	,,	1·35	,,	2·25	,,
Cider	,,	1·85	,,	3·90	,,

Hence the order in which these wines may be arranged, beginning with the least acid, is Sherry, Port, Champagne, Claret, Madeira, Burgundy, Rhine, Moselle.

(2.) The sugar was determined by means of Soleil's saccharometer, which at least gives the lowest limit to the amount of sugar.

The sweetness in different—

Sherries	varied from	4	grs. to	18	grs. in the ounce.
Madeira	,,	6	,,	20	,,
Champagne	,,	6	,,	28	,,
Port	,,	16	,,	34	,,
Malmsy	,,	56	,,	66	,,
Tokay	,,	74			,,
Samos	,,	88			,,
Paxarette	,,	94			,,

Claret, Burgundy, Rhine, and Moselle contained no sugar.

Hence the order in which these wines may be arranged, beginning with the driest, is—

Claret Burgundy Rhine Moselle
Sherry
Madeira
Champagne
Port
Malmsy
Tokay
Samos
Paxarette.

In a dietetic view, assuming that the sugar becomes acid, then the mean results as to the acidity of the different fluids examined, beginning with the least acid, is—

Geneva Whisky
Rum
Brandy
Claret
Burgundy
Rhine wine
Moselle
Sherry
Madeira
Champagne
Cider

Port
Porter
Stout
Malmsy Madeira
Ale
Tokay.

(3.) The alcohol was determined by means of the alcoholometer of M. Geisler of Bonn.

The strength of different samples of—

Port	varied from	20·7	per cent. to	23·2	per cent. by measure.
Sherry	,,	15·4	,,	24·7	,,
Madeira	,,	19·0	,,	19·7	,,
Marsala	,,	19·9	,,	21·1	,,
Claret	,,	9·1	,,	11·1	,,
Burgundy	,,	10·1	,,	13·2	,,
Rhine wine	,,	9·5	,,	13·0	,,
Moselle	,,	8·7	,,	9·4	,,
Champagne	,,	14·1	,,	14·8	,,
Brandy	,,	50·4	,,	53·8	,,
Rum	,,	72·0	,,	77·1	,,
Geneva	,,	49·4			,,
Whisky	,,	59·3			,,
Cider	,,	5·4	,,	7·5	,,
Bitter ale	,,	6·6	,,	12·3	,,
Porter	,,	6·5	,,	7·0	,,
Stout	,,	6·5	,,	7·9	,,

The Burgundy and Claret have less alcohol than was found by Mr. Brande forty years ago in the wines he examined. The Sherry is now stronger, the Port is not so strong, the Marsala is weaker, the Rhine wine is the same strength, the Brandy is as strong as formerly; the Rum is nearly half as strong again; the Porter is stronger, and the Stout rather stronger than formerly.

Lastly, the specific gravity of each liquid was taken. As this however chiefly depends on the amount of alcohol and sugar present, and as these were directly determined, the specific gravity may be taken as a distant control on the amount of sugar present.

Thus, in those wines in which the amount of alcohol was the same, the specific gravity was found to vary with the amount of sugar found by the saccharometer.

The results of the analysis of each sample of wine, &c. is given in a series of tables, which do not admit of any abstract.

PATENTS.

Patent granted to G. Shand *and* A. McLean, *for Improvements in obtaining Products from Tar.*

This invention has reference to the treatment of tar, for the purpose of extracting its products, and rendering the same available

for useful purposes, whether the tar to be so treated be obtained from wood, coal or animal substances.

In order to accomplish these objects, the tar is submitted to the following processes:—In the first place, crude or rough naphtha and ammonia is distilled over in the usual way from coal or gas tar; and by further distillation, "pitch oil," "tar oil," or "creosote oil" is obtained, which the patentees denominate crude "naphthaline oil." Secondly, this oil is purified by means of acids and alkalies, in the manner hereafter described; and from the oil so purified, the naphthaline, and also a lighter and a heavier oil, is extracted. And, lastly, tar obtained from wood or animal substances is submitted to the same processes, to extract therefrom the crude oil, to purify it, and to separate from it the purified oils and the denser substances contained therein. In order to carry into effect the first series of processes, forming part of this invention, the patentees take coal or gas tar, and put it into a still of any suitable construction, with a worm and condensing apparatus attached thereto, and by means of steam passed into the still from a steam-boiler, the crude or rough naphtha is distilled over in the usual way until the crude naphtha coming over from the still becomes of the specific gravity of about 910° (water being considered 1000°). The steam is then shut off, and by the application of heat from a fire, a quantity of water is distilled over, as well as the previously-mentioned naphthaline oil, which is commonly called pitch oil, tar oil or creosote oil. The distillation is still continued until the oil reaches the specific gravity of about 990°; the fire is then withdrawn, and the residue of the pitch in the still is run off in a heated state, and allowed to cool in the usual way. A further quantity of oil may be extracted from the pitch by subjecting it to a strong fire-heat in a retort, with a worm and condensing apparatus attached thereto.

The second part of the process relates to the purification of the crude naphthaline oil, and the extraction therefrom of the naphthaline and oils which it contains. For this purpose the crude naphthaline oil is put into a leaden vessel, and to every 100 gallons thereof about 15 gallons of sulphuric acid, of the specific gravity of about 1·830, is gradually added, the mixture being continually stirred until the acid has become mixed with all the impurities with which it can combine. The contents of the vessel are then allowed to settle, and the clear liquor is drawn off into another vessel. To every 100 gallons of oil about 10 gallons of caustic alkali, having the specific gravity of about 1·350, is next gradually added; and this mixture is kept continually stirred, until any excess of acid left in the oil is neutralized, and all other impurities with which the alkali can combine are taken up. The contents of the vessel are then allowed to settle, and the clear liquor is drawn off and put into a still of any convenient construction, with a worm and condensing apparatus attached.

The process of distillation is carried on until the oil coming over reaches the specific gravity of about 940°. The oil from the still is then run into a second vessel (leaving the former product of distil-

lation in the manner hereinafter described); and the process of distillation is continued until the contents of the still are run off. The oil, so distilled, is next treated with a small quantity of caustic ammonia, in a dry state, for the purpose of absorbing any trace of water remaining in it. When the oil has been allowed to settle, and has undergone filtration, it is ready for use, either alone or mixed with other oils. This manufacture of oil the patentees denominate "purified heavy naphthaline oil."

The inventors then take the former product of the distillation of the crude naphthaline oil before mentioned, and put it into any convenient still, with a worm and condensing apparatus attached, and to every gallon of oil about 1 lb. weight of caustic lime, or burnt lime-shells, are added. The oil and lime, having been well stirred together, are acted on by a gentle heat from a fire; and a light volatile oil is distilled over, which is afterwards rectified by means of steam from a steam-boiler, and passed into any suitable still, with a worm and condensing apparatus attached. This manufacture of oil is useful for solvent and other purposes. The distillation is still continued until the product reaches the specific gravity of about 910°, when a stronger heat is applied from the fire, and the oil is run from the still into a second vessel, the operation being continued until the contents of the still are distilled over. The oil last distilled is then allowed to cool down to a temperature of from 30° to 40° F., when the naphthaline will be deposited at the bottom of the vessel, and may be separated from the oil by filtration and pressure. The oil from which the naphthaline has been separated, and which is called by the patentees "light naphthaline oil," is treated with magnesia or other substance, in a dry state, to absorb any trace of water, and when filtered is ready for use. Naphthaline may also be obtained by treating the purified heavy naphthaline oil with caustic lime, in the manner above described. In order to purify the naphthaline, after it has been separated from the naphthaline oil, the naphthaline is put into a retort, or any convenient apparatus, and with a gentle heat it is sublimed in vapour into a wooden chamber, where it condenses in flakes of a white colour.

The last part of this invention consists in applying the series of processes above described to tar obtained from wood or animal substances. For this purpose the tar thus obtained is treated in a similar manner to that described in reference to the purification of crude naphthaline oil, and the heavier and lighter oils, and also the denser substances extracted and separated therefrom, such oils and denser substances being purified in the manner above described in reference to the heavier and lighter naphthaline oils and the naphthaline.—Sealed Nov. 5, 1852.

Patent granted to William Chisholm, *for Improvements in obtaining Caustic Soda, &c.*

In carrying out this invention, the patentee takes peat charcoal, and adds thereto an equal quantity of chloride of sodium. This

mixture is placed in a dry lime-purifier, and the gas is made to pass through it as through the lime now used; whereby the chloride of sodium is decomposed by the hydrosulphate of ammonia contained in the gas, and hydrochlorate of ammonia and hydrosulphate of soda are formed. The soluble salts thus obtained are separated from the mixture, either by passing steam through it or washing it with hot or cold water; the solution is then evaporated to dryness, and placed in the well-known apparatus for subliming sal-ammoniac. When heat is applied, the hydrochlorate of ammonia will be sublimed. The mixture may be subjected to this operation in the state in which it comes from the gas-works, that is, without the salts being first washed out; in such case, the mixture remaining in the retort, after subliming from it the hydrochlorate of ammonia, will be soda and charcoal. The soda must now be washed out, and evaporated or crystallized. The damp charcoal, from which the salts of ammonia and soda have been separated, may be again mixed with chloride of sodium. The sublimed hydrochlorate of ammonia, obtained as above, may be sold in the market; or the charcoal may be mixed with the chloride of sodium, and placed in a retort, and the hydrochlorate of ammonia obtained by sublimation mixed with rather more than its own weight of carbonate of lime, and placed in a second retort, connected with the former by a short and wide tube. A fire is to be lighted under the retort containing the hydrochlorate of ammonia and carbonate of lime, when the ammoniacal compound will be decomposed—the hydrochloric acid combining with the lime, and the ammonia with the carbonic acid. The volatile carbonate of ammonia will pass over into the retort containing the charcoal and chloride of sodium, and the chloride of sodium will then be decomposed, its chlorine combining with the ammonia, and the carbonic acid combining with the soda. The contents of the retort, which contained the ammonia and carbonate of lime, will now be chloride of calcium; and the contents of the retort which contains the charcoal must be treated as if the mixture had taken up the ammonia from purifying the gas. This process may be a continuous one, any little ammonia that may be lost in the process of manufacture being made good by a supply of the purifying mixture that has been used at the gas-works. Instead of carbonate of lime being used in one of the retorts, as described, lime may be used, when caustic ammonia will pass over instead of a carbonate; in this case a continuous stream of carbonic acid must be conducted into the retort containing the charcoal and chloride of sodium during the operation. Instead of using the purifying material which has been charged with ammonia from the purification of gas, a commercial muriate, or other salt of ammonia, may be used—such ammonia being of the same weight as the chloride of sodium acted upon. The operation will be precisely the same, the ammonia being always recovered, and capable of being used as often as may be required. —Sealed October 19, 1852.

THE CHEMICAL GAZETTE.

No. CCLXXI.—February 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Estimation of Urea, and a Method for the Determination of this Substance and Chloride of Sodium in the Urine. *By* Prof. LIEBIG.

THE author first describes three compounds of urea with peroxide of mercury. The former substance is here represented by U.

$2HgO + U$.—This was described by Dessaignes shortly after the publication of the author's first notice upon urea and peroxide of mercury*. Peroxide of mercury, suspended in water, and mixed with a warm solution of urea, becomes dissolved at first; if more be added, it is converted into a white powder, which when dried *in vacuo* becomes slightly yellow.

Heated when dry in a tube, the compound is decomposed, without deflagration, into ammonia and metallic mercury; mellone remains, which when further heated disappears with evolution of gaseous cyanogen.

When peroxide of mercury is digested on the water-bath with a solution of urea, some ammonia always escapes, and the resulting solution then contains some cyanate of peroxide or protoxide of mercury. The yellowish-white powder formed dissolves in prussic acid and muriatic acid, leaving a black residue of metallic mercury, with a slight evolution of gas; this solution, treated with milk of lime, evolves ammonia. This is the character of the cyanates. By longer digestion on the water-bath, the compound of urea loses its whitish colour, and becomes granular and citron-yellow; this latter compound behaves like a basic cyanate of mercury. Analysis gave for 100 parts of $2HgO + U$—

Peroxide of mercury	81·09
Urea	21·45

By exactly the same process, the author sometimes also obtained the following compound, by digesting a solution of urea containing 10 per cent. of urea with peroxide of mercury.

$3HgO + U$.—This compound is precipitated from a solution of urea which has been rendered alkaline by potash, by the addition of a solution of bichloride of mercury; the liquid must be kept alkaline by fresh additions of potash. The precipitate is gelatinous and snow-white; when put into boiling water, after complete washing, it

* Chem. Gaz., vol. x. p. 37.

becomes converted into a sandy, granular, yellow or yellowish-white powder. The water in this case becomes alkaline, and takes up urea.

When dry, this substance is a reddish-yellow powder, which when heated is decomposed with a crackling, and in a moist state with an explosion. When this decomposition is effected in the dark, light is produced, and beautiful green sparks are observable; water and carbonate of ammonia are eliminated, and metallic mercury is sublimed, generally without any residue of mellone; the compound dissolves with effervescence in hydrocyanic and muriatic acids, and alkalies produce a white precipitate in the solution in the latter acid. Analysis:—

HgO....	84·1	84·3	83·91	84·0	..	..	3=324	84·37
U.....	..	..	..	..	15·6	16·6	1 60	15·63

4HgO + U.—This compound is produced when, instead of the bichloride, the pernitrate of mercury is employed as above described. This is also exactly like the preceding compound in its behaviour. The analysis of the substance, dried over sulphuric acid, gave—

HgO	87·82	87·3	88·72	87·4	4=432	87·804
U	..	12·7	10·96	..	1 60	12·196

Oxide of Silver and Urea, 3AgO + U.—Freshly precipitated oxide of silver is gradually converted, in a solution of urea at 104°–122° F., into a gray powder, which has a crystalline appearance under the microscope. The crystals are transparent, colourless prisms. This substance dissolves readily in nitric acid, without any evolution of gas; it dissolves with difficulty in ammonia; when it is touched with a red-hot body, it burns like tinder, with a strong evolution of ammonia, into a darker-coloured coherent mass, which effervesces with acids; and when treated with nitric acid, evolves, together with carbonic acid gas, nitrous oxide or nitrous acid gas. If the burnt mass be heated in a tube, the odour of cyanic acid is perceived, and a white substance with the properties of cyamelide sublimes. The compound becomes converted by the first burning into a mixture of metallic silver and protocyanate of silver. When heated in the tube, a second ignition is produced, and the cyanate of protoxide of silver is decomposed, a portion of the cyanogen escaping in the form of cyanic acid, whilst another portion remains with the silver. Analysis gave—

AgO	..	84·32	84·54	84·81	83·50	84·68	84·75	3=348	85·29
U	14·25	..	..	..	..	..	..	1 60	14·71

Solutions of nitrate of the peroxide of mercury and urea furnished different compounds according to the proportions in which they were mixed.

Nitrate of Peroxide of Mercury and Urea, 4HgO + NO^5, U.—This compound is produced when the two solutions are much diluted and mixed warm. The precipitate, when it remains in the fluid, soon becomes converted into a heavy white powder, which under the microscope appears to consist of small needles grouped concentrically. Analysis gave—

NO^5.....	..	..	9·55	1 =	54	9·90
U	..	..	10·95	1	60	10·98
HgO	78·58	79·14	..	4	432	79·12

Second Salt, $2HgO+NO^5$, U.—This salt is produced when a solution of crystallized nitrate of urea is poured into a moderately dilute solution of pernitrate of mercury, with a little nitric acid added to it, until a slight permanent turbidity appears. The fluid is filtered and allowed to stand, when crystalline crusts are deposited, consisting of an aggregation of small, rectangular, shining, transparent tables. These crystals are decomposed by treatment with boiling water; they become dull and opake, and pass into the preceding compound, the water extracting nitrate of urea. Analysis furnished:—

NO^5	..	..	16·1	1 =	54	16·37
U	..	..	18·9	1	60	18·18
HgO.....	65·6	65·7	..	2	216	65·45

Third Salt, $3HgO+NO^5$, U.—This is produced when a dilute solution of pernitrate of mercury is added to a solution of urea as long as a precipitate is formed, and the whole then left standing in a temperature of 104°–122° F. Under the microscope the precipitate is found to be principally composed of six-sided prisms, amongst which are some roundish grains and a few square prisms of the preceding compounds.

Quantitative Determination of Chlorine and Chlorine Compounds, especially Chloride of Sodium, by means of the Pernitrate of Mercury.

A solution of urea is not precipitated by solution of bichloride of mercury, whilst pernitrate of mercury immediately produces a thick white precipitate. The chlorine compounds of the alkalies become completely converted by pernitrate of mercury into bichloride of mercury and a nitrate of the alkaline base.

Solution of chloride of sodium, however, when mixed with nitrate of mercury, solidifies into a laminated mass of bichloride of mercury. When chloride of sodium has been added to a solution of urea, the addition of nitrate of the peroxide of mercury only produces a precipitate when all the chloride of sodium has been converted into bichloride of mercury, but then every drop of the nitrate produces a permanent turbidity.

Hence it is evident that upon this behaviour a method of determining chlorine, chloride of sodium, &c. and mercury may be established; for if the quantity of mercury in the solution of nitrate of mercury be ascertained, the quantity of the latter which has to be added to a solution of urea containing an unknown quantity of chloride of sodium for the production of a permanent precipitate, will give the quantity of chlorine or chloride of sodium in the solution. If, on the other hand, the quantity of chloride of sodium contained in a solution of urea be known, and the quantity of mercury in its solution unknown, the amount of mercury in the requisite quantity of the mercurial solution may be readily calculated. This process

for the determination of chloride of sodium is especially adapted for urine, as there is no occasion to add urea to this; it may serve equally well in the determination of the quantity of chlorine contained in a salt spring or in sea-water, particularly when a considerable number of such examinations have to be performed. In those cases in which, instead of urine, the chloride of sodium is to be determined in other neutral fluids, this method must be varied in some respects.

Preparation of the Pernitrate of Mercury.—The best plan is to dissolve 1 part of pure mercury in 5 parts of nitric acid of spec. grav. 1·425; it is heated, and a few drops of nitric acid added to it until no more red fumes are evolved, and the solution no longer becomes turbid with chloride of sodium; it is then evaporated to a syrup. Impure mercury, containing lead or bismuth, must not be employed. If the mercury be impure, pure nitrate of protoxide of mercury is first prepared by recrystallization, and this converted into the pernitrate.

The mercurial solution which is to be employed in the determination of chloride of sodium must be of known strength; this may be ascertained either directly, or the quantity of mercury contained in it is determined, and it is then diluted with water until a cubic centimetre of the mercurial solution will exactly indicate 10 milligrms. of the chloride. In both cases a solution of chloride of sodium of known strength is necessary.

The author states that such a solution may very readily be prepared without weighing by saturating water at 54°–75° F. with pure transparent lumps of rock-salt. From 10 cub. centims. of this solution the author obtained 3·185, 3·184, 3·195, 3·175, or on the average 3·184 grms. of chloride of sodium as a residue after evaporation. This agrees exactly with the experiments of Fuchs and Fehling.

If now 20 cub. centims. of this solution be mixed with 298·4 cub. centims. of water, 318·4 cub. centims. of dilute solution of chloride of sodium are obtained, containing 6368 milligrms. of chloride of sodium. 10 cub. centims. of this solution consequently contain 200 milligrms. of chloride of sodium.

Preparation of the Test Fluid for the Determination of Chloride of Sodium.—By means of a small pipette, which contains exactly 10 cub. centims. of fluid up to the line on the narrow tube, that quantity of the solution of chloride of sodium just described is measured, and allowed to run into a small beaker; 3 cub. centims. of a solution of urea, of which 100 cub. centims. contain 4 grms. of urea, so that 3 cub. centims. will contain 40 milligrms. are then added.

The diluted mercurial solution, the strength of which is to be determined, is put into a minim glass, and dropped into the solution of chloride of sodium to which the urea has been added, and which is kept constantly rotating. As soon as a distinct permanent precipitate is produced in the fluid, the testing is completed.

If with 10 cub. centims. of the solution of chloride of sodium, 7·8 cub. centims. of the mercurial solution are required for the produc-

tion of a precipitate, the latter fluid is too concentrated to furnish an exact valuation; it must be diluted with an equal volume of water, and the testing performed a second time. If it be supposed that 15·5 cub. centims. of this mercurial solution are now required for the production of turbidity in the solution of chloride of sodium with urea, then to every

155 volumes of the mercurial solution
45 volumes of water are added, by which means

200 volumes of a mercurial solution are obtained, of which 20 cub. centims. will indicate exactly 200 milligrms., or 1 cub. centim. 10 milligrms. of chloride of sodium.

If, in the first testing, 10 cub. centims. of the solution of chloride of sodium require only 2·7 cub. centims. of the mercurial solution, five or six times the volume of water must be added to the latter before the final valuation. The concentration of the mercurial solution to be valued must not be too far from the desired strength.

Lastly, the correctness of the measurements is to be checked; and the degree of permanent turbidity obtained by the addition of 20 cub. centims. of the test fluid to 10 cub. centims. of the solution of chloride of sodium with urea must be carried in the eye; for in the employment of this test fluid in the quantitative determination of chloride of sodium, the addition of too much or too little of the mercurial solution, by which the turbidity is rendered stronger or weaker, is a source of error, which however is readily got rid of by practice.

The above-described test fluid is calculated for those cases in which no foreign salts and no excess of urea is present in the solution with the metallic chlorides; but when employed in the determination of the chloride of sodium in the urine, it gives a slight error, by which the quantity contained in that fluid appears to be less than it really is. This error is caused by the turbidity, making its appearance somewhat earlier when much urea and foreign salts are present, as the precipitate is rather more difficult of solution in such fluids. A deposit of nitrate of mercury and urea is not produced in the fluid until this is saturated with it; the mercurial solution always contains free nitric acid, which dissolves more of it than water, and this more than a solution of nitrate of urea. Now as urine generally contains more urea than was added to the solution of chloride of sodium for the purpose of valuing the mercurial solution, this urea seizes upon a portion of the free nitric acid of the mercurial salt, forming nitrate of urea, by which the solvent power of the fluid for the precipitate is diminished; and this makes its appearance sooner, so that a little less of the test fluid is required for the production of the reaction. This error may be entirely prevented, if to the 10 cub. centims. of solution of chloride of sodium, which has been mixed with 3 cub. centims. of solution of urea, 5 cub. centims. of a cold saturated solution of sulphate of soda be added, and the test fluid then valued.

Nitrate of mercury gives a yellow pulverulent precipitate with sulphate of soda. When the sulphate of soda contains chloride of

sodium, the addition of the nitrate of mercury does not produce this precipitate until the whole of the chloride of sodium is converted into bichloride of mercury; the experiment consequently is only affected by the addition of the solution of sulphate of soda in that the free acid of the mercurial salt combines with the sulphate of soda to form an acid salt, by which means the same object is attained as by an excess of urea.

If urea be mixed with a solution of sulphate of soda free of chloride of sodium, and then nitrate of mercury be added to the mixture, it thickens, even when the solutions are tolerably diluted, into a snow-white compound, forming a gelatinous mass, which contains sulphuric acid, urea and peroxide of mercury; this is a little more difficult of solution in water and nitric acid than the corresponding nitric acid compound.

The method just described for the determination of chlorine does not yield in exactitude to that by means of silver salts; but it is only adapted for neutral or slightly acid or alkaline fluids, an excess of acid opposing the formation of the precipitate.

When it is desired to determine the amount of chloride of sodium in urine, the phosphoric acid must first be got rid of. This is effected by a mixture of 1 vol. of a cold saturated solution of nitrate of baryta with 2 vols. of cold saturated baryta water. Of this mixture, 1 or 2 vols. are added to the urine under examination; the liquid is filtered from the precipitate, and neutralized by nitric acid. For investigation, 15 cub. centims. of this fluid, corresponding to 10 cub. centims. of urine, is measured in a small pipette, which exactly contains it; then poured into a small beaker and mixed, by constant stirring, with the mercurial solution. After the production of the turbidity, the quantity of fluid poured from the minim glass is ascertained; every cubic centimetre employed represents 10 milligrms. of chloride of sodium. As a proof of the exactitude of the method, the author gives the following comparative results obtained with a silver solution, which was also adjusted to a solution of 10 milligrms. of chloride of sodium in 1 cub. centim. of water:—

	With nitrate of silver. milligrms.	With nitrate of mercury. milligrms.
1. 10 c. c. of urine, collected in the morning..	115·4	115·0
2. 10 c. c. of urine, collected in the morning from a child.....	110·0	110·0
3. 10 c. c. of urine, passed after eating	164·0	164·0
4. 10 c. c. of urine, passed before dinner	189·0	188·5
5. 10 c. c. of urine, passed before dinner	74·0	74·0
6. 10 c. c. of urine, passed before dinner	142·8	142·8
7. 10 c. c. of urine, passed after tea-drinking..	127·5	127·5
8. 10 c. c. of urine, passed after drinking beer	27·7	27·7
9. 10 c. c. of urine, passed before bed-time, after drinking beer.....	25·0	25·0
10. 10 c. c. of the same urine	25·0	25·0
11. 12. 10 c. c. of urine, from a female	110·0	110·0

When the presence of urea is to be ascertained in urine, the chloride of sodium contained in it produces an error, which may be avoided by a preliminary precipitation of the chlorine. For this purpose the method of determination of chloride of sodium by means of nitrate of mercury should be employed to ascertain exactly the quantity of silver solution necessary to precipitate the whole of the chlorine.

[To be continued.]

On Sulphuret of Phosphorus. *By* Dr. W. Wicke.

If a piece of sulphur be laid upon a piece of phosphorus under water, the surfaces of contact of both bodies are changed; in the course of a few hours sulphuret of phosphorus runs down in oleaginous drops. If the phosphorus and sulphur be employed in the proportions of 8 : 2, the fluid pale yellow sulphuret of phosphorus, P^2S, is produced. This, when exposed to the sunlight, becomes opake immediately, but again becomes clear in the dark. Sulphur, employed in excess, furnishes a solution of sulphur in sulphuret of phosphorus, which, when shaken with solution of potash, becomes clear and refractive. When kept for a considerable time in a cool place, sulphur separates from it in good crystals. Sulphur and phosphorus, in the proportions of 2 : 4, do not produce PS, but P^2S. Sulphur remains free.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 115.

On some Compounds of Protoxide of Mercury with Nitrates. *By* G. Stædeler.

From a mixture of moderately-concentrated solutions of nitrate of the protoxide of mercury and nitrate of lead, a precipitate consisting of microscopic octahedral crystals is soon thrown down. Similar salts are furnished by the nitrates of baryta and strontia. These salts are colourless double salts when they crystallize from solutions containing a little nitric acid, and when the action of light is prevented during the crystallization. They acquire a faint yellowish colour when exposed to the light under the acid mother-liquor; when exposed to the action of the light in the dry state, the lead and baryta compounds soon become citron-yellow, and afterwards brownish-green. The strontia compound is nearly as sensitive to the action of light as chloride of silver; it becomes flesh-coloured when exposed only for a few moments to diffused daylight, and gradually changes its colour to a dingy brown. By recrystallization from hot water containing nitric acid, the compounds again become white.

The Lead Salt, $2(PbO, NO^5) + (Hg^2O)^2, NO^5$, has these peculiarities, that in its formation the neutral lead salt causes a splitting of the neutral nitrate of protoxide of mercury into basic and acid salt, and that the formation of this double salt is not obstructed by the presence of a great excess of nitric acid. If the salt be boiled with the acid mother-liquor from which it has been deposited, it is

dissolved unchanged, and on cooling shoots out into larger crystals. It acts in the same manner when boiled with dilute nitric acid. When pure water is poured over it, on the other hand, it splits, even whilst cold, into nitrate of lead and an amorphous, citron-yellow basic salt, which when heated becomes greenish. Its analysis gave—

PbO	27·91	27·97	2 =	223·12	27·85
Hg^2O	51·82	..	2	416·00	51·93
NO^5	20·27	..	3	162·00	20·22

The Baryta Salt, $2(BaO, NO^5)+(Hg^2O)^2, NO^5$, is produced in the same manner by the employment of nitrate of baryta instead of nitrate of lead. Its analysis gave—

BaO	20·86	2 =	152·64	20·89
Hg^2O	56·88	2	416·00	56·94
NO^5	22·26	3	162·00	22·17

The Strontia Salt, $2(SrO, NO^5)+(Hg^2O)^2, NO^5$, is much more readily soluble, and can therefore only be obtained from concentrated solutions. Analysis:—

SrO	15·31	2 =	103·84	15·23
Hg^2O	..	2	416·00	61·01
NO^5	..	3	162·00	23·76

The nitrates of lime, of silver, of peroxide of mercury, and of copper did not furnish similar double salts. The precipitate produced by sulphuric acid in the solution of nitrate of the protoxide of mercury is neutral sulphate of protoxide of mercury, Hg^2O, SO^3. —*Ann. der Chem. und Pharm.*, lxxxvii. p. 129.

On some peculiar Reductions of Metals in the Humid Way. *By* Prof. Wöhler.

The following experiments were made for Prof. Wöhler by Hiller. The observation first made by Bucholz, that long crystals of metallic tin are formed when a rod of that metal is inserted in a solution of protochloride of tin, and the latter carefully overlaid with water, was first of all further tested. It appeared that, for the production of large crystals, the solution of chloride of tin must be acid. Of the tin immersed in the solution there was always more dissolved than was made up by that which crystallized. In one experiment the proportions were as 7 : 6.

These crystals are formed at the point of contact between the two fluids. If the solution be neutral, they appear below this in the solution of the protochloride, and remain bright.

Copper, inserted into a neutral solution of nitrate of copper, covers itself entirely with brownish-red crystals of protoxide of copper, and afterwards with sharp crystals of metallic copper. The copper is dissolved, especially at the point of contact of the fluids. The same phænomenon is produced, but in a less degree, with sulphate of copper. In solution of perchloride of copper, the copper is covered with crystals of the protochloride.

A rod of zinc, under similar circumstances, covers itself with gray granules of metallic zinc, especially at its lower end. In this case also the zinc is dissolved at the point of contact of the fluids.

Cadmium behaves in a similar manner in the solution of its nitrate; the reduced metal is more pulverulent, and therefore much more readily oxidized in the air than the reduced zinc.

Lead, in a solution of neutral nitrate or acetate of lead, furnishes small shining crystals of lead.

Bismuth precipitates the metal from a solution of protochloride of bismuth, if the latter has been overlaid first with muriatic acid, and afterwards with water.

On silver, immersed in a concentrated solution of nitrate of silver overlaid with water, metallic silver is deposited in a dendritic form, always originating from a few scattered points of the surface of the silver.—*Ann. der Chem. und Pharm.*, lxxxv. p. 253.

On the Theory of the Amides. *By* A. Wurtz.

It has already been shown, by the researches of the author and Dr. Hoffmann, that many alkaloids might be regarded as derived from *ammonia*; and M. Gerhardt has pointed out that the acids are derived from the type *water*. The author here endeavours to show that the compounds known as *amides*, which have long been regarded as connected with the acids, are truly, like the latter, derived from the type *water*.

In adopting the equivalents generally employed, the monobasic acids must be regarded as derived from two molecules of water; the oxygen of these two molecules of water occupies, so to speak, a distinct place in the molecule of the acid itself, and must not be confounded with the oxygen contained in the complex group substituted for one of the molecules of hydrogen. These relations are, in fact, exactly expressed by writing the formula of acetic acid, for example, in the following manner:—

$$\left.\begin{matrix} C^4\,H^3\,O^2 \\ H \end{matrix}\right\} O^2.$$

This being settled, nothing is more easy than to explain the formation, and represent the constitution of the amides formed by the monobasic acids. Two molecules of hydrogen in the ammonia remove the two molecules of oxygen situated outside of the binary group, and the residue NH takes the place of this oxygen.

In this point of view, an amide is consequently nothing but an acid in which the 2 molecules of oxygen of the primitive type *water* have been replaced by the residue NH of a molecule of ammonia which has lost 2 equivs. of hydrogen. This substitution does not in any way modify the general form or the type of the compound, which remains perfectly intact. The following formulæ will show at a glance the simplicity of these relations:—

$$\left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}O^2, \qquad \left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}NH, \qquad \left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}N(C^4H^5)^*,$$

Acetic acid. Acetamide. Æthylacetamide.

$$\left.\begin{matrix}C^4H^3O^2\\C^4H^3O^2\end{matrix}\right\}O^2, \qquad \left.\begin{matrix}C^4H^3O^2\\C^4H^3O^2\end{matrix}\right\}NH\dagger, \qquad \left.\begin{matrix}C^4H^3O^2\\C^4H^3O^2\end{matrix}\right\}N(C^4H^5).$$

Anhydrous acetic acid. Diacetamide. Æthyldiacetamide.

It is evident that nothing prevents the substitution of a complex group for the hydrogen of the residue NH.

According to M. Gerhardt, the bibasic acids are derived from 2 molecules of water. In the notation generally adopted, it is necessary to make them derivatives of *two binary groups* of molecules of water. It may be supposed that in each of these groups one molecule of hydrogen is replaced by an acidifacient group; so that a bibasic acid may be regarded as formed by the union of two conjugate monobasic groups. In this way the constitution of oxalic acid will be expressed by the following formula:—

$$\left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}O^2,$$

$$\left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}O^2.$$

The amides of oxalic acid are formed by the intervention of 1 or 2 molecules of ammonia, and by the elimination of 4 or 2 molecules of water. On these principles, the constitution of these amides may be imagined to be as follows:—

$$\left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}O^2, \quad \left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}NH, \quad \left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}NH, \quad \left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}NH, \quad \left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}N(C^4H^5),$$

$$\left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}O^2, \quad \left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}NH, \quad \left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}O^2, \quad \left.\begin{matrix}C^2O^2\\C^4H^5\end{matrix}\right\}O^2, \quad \left.\begin{matrix}C^2O^2\\H\end{matrix}\right\}N(C^4H^5).$$

Oxalic acid. Dioxamide. Oxamic acid. Oxamethane. Diæthyloxamide.

Succinic acid, another bibasic acid, may be regarded as containing two monobasic groups, ($C^4H^2O^2$). When 2 equivs. of ammonia react upon this acid, the action produces, in consequence of the elimination of 4 molecules of water, the compound which may be called *disuccinamide*, When, on the other hand, the formation of 4 equivs. of water is caused by the action of a single equivalent of ammonia upon the succinic acid, the hydrogen of the ammonia is not sufficient for the formation of this water. Under these conditions the molecule of ammonia only loses 2 equivs. of hydrogen, to which the 2 equivs. of basic hydrogen of the two succinic groups unite. In this manner the *succinimide* of Laurent and Gerhardt is obtained; this was improperly named *bisuccinamide* by

* The substance formed by the action of æthylamine on acetic æther is identical with that formed by the action of cyanic æther on acetic acid. The composition has not been ascertained by analysis; but as caustic potash splits it into acetic acid and æthylamine, it may be regarded as æthylacetamide.

† It is very easy to prepare this compound by passing vapours of hydrated cyanic acid into anhydrous acetic acid.

F. d'Arcet. The following formulæ express the constitution of these amides :—

$$\left.\begin{matrix}C^4H^2O^2\\H\end{matrix}\right\}O^2, \qquad \left.\begin{matrix}C^4H^2O^2\\H\end{matrix}\right\}NH, \qquad \left.\begin{matrix}C^4H^2O^2\\C^4H^2O^2\end{matrix}\right\}NH,$$

Succinimide.

$$\left.\begin{matrix}C^4H^2O^2\\H\end{matrix}\right\}O^2, \qquad \left.\begin{matrix}C^4H^2O^2\\H\end{matrix}\right\}NH,$$

Succinic acid. Disuccinamide.

The constitution of the amides of carbonic acid, as a final example, may be expressed as follows :—

$$\left.\begin{matrix}CO\\H\end{matrix}\right\}O^2, \quad \left.\begin{matrix}CO\\H\end{matrix}\right\}NH, \quad \left.\begin{matrix}CO\\H\end{matrix}\right\}NH, \quad \left.\begin{matrix}CO\\H\end{matrix}\right\}NH, \quad \left.\begin{matrix}CO\\H\end{matrix}\right\}N(C^5H^5),$$

$$\left.\begin{matrix}CO\\H\end{matrix}\right\}O^2, \quad \left.\begin{matrix}CO\\H\end{matrix}\right\}NH, \quad \left.\begin{matrix}CO\\H\end{matrix}\right\}O^2, \quad \left.\begin{matrix}CO\\C^4H^5\end{matrix}\right\}O^2, \quad \left.\begin{matrix}CO\\C^4H^5\end{matrix}\right\}O^2.$$

Carbonic acid (hypothetical hydrate). Carbamide. Carbamic acid. Urethane. Æthylurethane.

Carbonic acid is consequently to be regarded as a bibasic acid, derived from two groups of molecules of water.

Only a small number of amides derived from the tribasic acids have been obtained. To show how readily they may be made to enter the circle just traced, the author gives his idea of the constitution of the anilides of citric acid obtained by M. Pebal. The hydrogen of the residue NH, which appears in all the preceding formulæ, is here replaced by phenyle, $C^{12}H^5$:—

$$\left\{\begin{matrix}\left.\begin{matrix}C^4H^2O^3\\H\end{matrix}\right\}O^2\\ \left.\begin{matrix}C^4H^2O^3\\H\end{matrix}\right\}O^2\\ \left.\begin{matrix}C^4H\ O^2\\H\end{matrix}\right\}O^2\end{matrix}\right. \qquad \left\{\begin{matrix}\left.\begin{matrix}C^4H^2O^3\\H\end{matrix}\right\}N(C^{12}H^5)\\ \left.\begin{matrix}C^4H^2O^3\\H\end{matrix}\right\}N(C^{12}H^5)\\ \left.\begin{matrix}C^4H\ O^2\\H\end{matrix}\right\}N(C^{12}H^5)\end{matrix}\right. \qquad \left\{\begin{matrix}\left.\begin{matrix}C^4H^2O^3\\C^4H^2O^3\end{matrix}\right\}N(C^{12}H^5)\\ \left.\begin{matrix}C^4H\ O^2\\H\end{matrix}\right\}N(C^{12}H^5)\end{matrix}\right.$$

Citric acid. Citranilide. Citrobianile.

$$\left\{\begin{matrix}\left.\begin{matrix}C^4H^2O^3\\H\end{matrix}\right\}N(C^{12}H^5)\\ \left.\begin{matrix}C^4H^2O^3\\H\end{matrix}\right\}O^2\\ \left.\begin{matrix}C^4H\ O^2\\H\end{matrix}\right\}O^2\end{matrix}\right. \qquad \left\{\begin{matrix}\left.\begin{matrix}C^4H^2O^3\\C^4H^2O^3\end{matrix}\right\}N(C^{12}H^5)\\ \left.\begin{matrix}C^4H\ O^2\\H\end{matrix}\right\}O^2.\end{matrix}\right.$$

Bibasic citromonanilic acid, formed by the elimination of 2 molecules of water.

Monobasic citromonanilic acid, formed by the elimination of 4 molecules of water.

The preceding observations apply more particularly to the most ordinary mode of formation of the amides, that is to say, to the action exerted by ammonia itself, or to the action of heat upon an ammoniacal salt. The author now shows that the views enounced agree perfectly with the other modes of formation of the amides.

1. When ammonia reacts upon a compound æther, such as acetic

æther, it takes up the 2 molecules of oxygen which are outside the groups; 2 molecules of water are formed, which react by double decomposition on the two groups of the æther, so as to give origin to an amide and an alcohol. The reaction consequently is resolvable into two phases, as shown by the following formulæ:—

$$\left.\begin{matrix}C^4H^3O^2\\C^4H^5\end{matrix}\right\}O^2+NH^3=\left.\begin{matrix}C^4H^3O^2\\C^4H^5\end{matrix}\right\}NH+2HO$$

Acetic æther.

$$\left.\begin{matrix}C^4H^3O^2\\C^4H^5\end{matrix}\right\}NH+2HO=\left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}NH+\left.\begin{matrix}C^4H^5\\H\end{matrix}\right\}O^2.$$

Acetamide. Alcohol.

2. When ammonia reacts upon the chloride of an oxygenated radical, 2 molecules of hydrogen are separated from the ammonia; one of these with the chlorine forms muriatic acid, which is eliminated; the other replaces the chlorine, and the residue NH combines with the binary group modified by the substitution,—

$$\left.\begin{matrix}C^{14}H^5O^2\\Cl\end{matrix}\right\}+NH^3=ClH+\left.\begin{matrix}C^{14}H^5O^2\\H\end{matrix}\right\}NH.$$

Chloride of benzoyle. Benzamide.

3. When cyanic æther $\left.\begin{matrix}C^2N\\C^4H^5\end{matrix}\right\}O^2$ reacts on a hydrated or anhydrous acid, on anhydrous acetic acid for instance, the carbon of the cyanogen combines with the oxygen of the æther and of the acid; carbonic acid is evolved, and the residue $N(C^4H^5)$ of the æther attaches itself to the two groups of the anhydrous acetic acid,—

$$\left.\begin{matrix}C^2N\\C^4H^5\end{matrix}\right\}O^2+\left.\begin{matrix}C^4H^3O^2\\C^4H^3O^2\end{matrix}\right\}O^2=C^2O^4+\left.\begin{matrix}C^4H^3O^2\\C^4H^3O^2\end{matrix}\right\}N(C^4H^5).$$

Cyanic æther. Anhydrous acetic acid. Æthyldiacetamide.

By adopting these views of the constitution of the amides, the acid properties exhibited by some of these bodies may be satisfactorily explained. Thus it is evident that oxamic acid must be an acid and a monobasic acid, since it contains one of the two monobasic groups of oxalic acid. It may be very readily imagined, besides, that even those amides which have hitherto been regarded as neutral, and which do not contain oxygen outside the conjugate groups, may, under certain circumstances, exchange the basic hydrogen of the primitive groups of the acid, or even the hydrogen of the residue NH, not only for an organic group, but even for a metal. —*Comptes Rendus*, August 8, 1853, p. 246.

On the Presence of Formic Acid in the Human Secretions. *By* DUGALD CAMPBELL, *Analytical Chemist to the Brompton Hospital, &c.**

In my former communication upon this subject†, it will be noticed that no acids whatever were used by me either upon the vomits or urine, to distil from the former the formic acid and from the latter the formiate of ammonia. My object in avoiding acids was to pre-

* Communicated by the Author.

† Chem. Gaz., vol. xi. p. 310.

clude its being said, that, by their action with heat upon the substances I examined, I had assisted in the formation of the formic acid; although, for my own part, I do not see any objection to the use, especially with care, of the inorganic acids not easily decomposable by organic substances with heat, such as phosphoric acid, and likewise of several of the stronger organic acids, such as tartaric acid.

Not using an acid to liberate the formic acid in the urine caused the experiments* to be very much more bulky and tedious than they otherwise would have been. A pint of urine in a retort, acidified by either phosphoric or tartaric acid, and distilled carefully by a water-bath, will yield sufficient formic acid to be detected by all ordinary tests.

The operator should observe that the urine in the retort is acid at the conclusion of the experiment, or the distillate may be tested from time to time by sensitive litmus-paper; if found alkaline, the heat must be withdrawn, and when the contents have cooled considerably, more acid added to the retort. A good deal of trouble may be saved by having, in place of the stopper of the retort, a perforated cork with a thistle-funnel passing to nearly the bottom of the liquid, and by this means adding the acid gradually if the liquid comes over alkaline, as stated before.

I have been engaged for some time back in the examination of blood of phthisical patients before, during, and after different treatment, for an investigation not my own, and with a different object in view than the detection of formic acid; still I thought it would be an interesting fact to pronounce whether formic acid is or is not to be found in blood.

The quantity of blood which I had to operate upon was necessarily very small; little more than half an ounce from each patient. The serum fortunately was not much required for my other investigations, and was what I alone wanted, so I was able to collect a few ounces; and before it became putrid, I acidified it, and distilled it in a retort by means of a water-bath. Whether I acidified with phosphoric or tartaric acid, the results I obtained were the same. The distillate, treated as I have stated in my last paper†, when acting upon the acid liquid from the vomit, will yield an acid with all the properties corresponding to formic acid.

The only other opportunity which I had of examining blood was from a woman said to be healthy, otherwise than in a tendency of flow of blood to the head. In this I found formic acid likewise, but as far as I could judge by qualitative tests, not in such quantity as in the blood of the phthisical patients first examined.

Quality Court, Chancery Lane, January 1854.

On the supposed Conversion of Ammonia into Nitric Acid in the Animal Organism. *By* CHRISTIAN JAFFÉ.

A series of experiments have recently been made known by Dr. Bence Jones, from which it is inferred, that after introducing into

* Chem. Gaz., vol. xi. p. 312. † *Ibid.*, vol. xi. p. 311.

the stomach a large quantity of ammoniacal compounds, nitric acid appears in the urine as a product of their oxidation.

From the extreme apparent improbability that such an oxidation could be effected in the animal organism, and at the instigation of Prof. Lehmann, the author has repeated the experiments upon which this inference is founded; and has come to the conclusion, that the method which Dr. Bence Jones adopted for detecting the presence of nitric acid in the urine is altogether inapplicable, and consequently that the inference that ammonia is oxidized within the organism is perfectly unfounded.

The method consists in distilling the somewhat concentrated urine with concentrated sulphuric acid until about one-half or two-thirds have passed over, treating the distillate with carbonate of potash, evaporating and testing the residue for nitric acid by means of starch, iodide of potassium and dilute hydrochloric acid, or with indigo.

The author believes that this process is inapplicable, because, even admitting the presence of nitric acid, it would appear impossible to distil over this acid in the presence of urea, or indeed any other organic substance. In order to decide this point, the author added a few drops of nitric acid to normal urine, concentrated by evaporation, and then distilled with sulphuric acid. The distillate, treated with starch and iodide of potassium, gave a reaction, which, although readily accounted for by subsequent experiments, at first led the author to form the erroneous opinion that a distillation of undecomposed nitric acid from urine actually took place. Normal urine, distilled with concentrated sulphuric acid, gave a liquid which became intensely blue when treated with starch and iodide of potassium, while at the same time it gave no indication of nitric acid with protosulphate of iron. It soon became evident that this reaction was altogether owing to the presence of sulphurous acid, formed by the action of the sulphuric acid upon the organic substances, and which, as is well known, causes a separation of iodine. It thus becomes easily intelligible why Dr. Bence Jones so seldom obtained this reaction in normal urine, as he saturated the distillate with carbonate of potash, and evaporated.

The presence of sulphurous acid in the distillate, and the dependence of the reaction upon it, was demonstrated in the following manner:—

In the first instance, normal urine was distilled without any addition of acid; and, as was to be expected, the distillate gave no reaction. Normal urine was then distilled with sulphuric acid; the distillate gave a reaction with starch and iodide of potassium; when tested with protochloride of tin for sulphurous acid, it acquired a yellow colour, but even on boiling no precipitate was formed, a result which might fairly be attributed to the small quantity of sulphurous acid. In order to prove more decisively that the reaction was owing to this small quantity of sulphurous acid, normal urine was distilled with phosphoric instead of sulphuric acid; and the distillate when tested did not give the slightest trace of a reaction.

Lastly, when a distillate which at first gave the reaction was allowed to stand twenty-four fours, it no longer gave it, but the presence of sulphuric acid could be distinctly ascertained.

Thus then it appears that an oxidation of ammonia to nitric acid in the animal organism has not by any means been proved by Dr. Bence Jones's experiments. It remained, therefore, necessary to ascertain by some other means whether such a formation of nitric acid really took place. For this purpose, concentrated urine, mixed with a few drops of nitric acid, was distilled with phosphoric acid; and the distillate did not give the slightest reaction either with starch and iodide of potassium or with protosulphate of iron.

After these results, the author considers it unnecessary to enter more fully upon the consideration of the various deductions from Dr. Bence Jones's experiments; such, for instance, as the assumed formation of nitric acid from urea introduced into the stomach, especially as Frerich has already proved that this is always attended by an increase in the quantity of urea in the urine.—*Journ. für Prakt. Chem.*, June 1853; and *Pharmaceutical Journal*, Nov. 1, 1853.

On the Crystalline Hydrate of Oxide of Iron.
By MM. LIMBERGER *and* WITTSTEIN.

It is well known that the officinal hydrated oxide of iron becomes crystalline under certain circumstances, and is then less efficacious as an antidote in poisoning by arsenic.

Limberger has observed that this result is produced not only by the lapse of time, but much more rapidly when this preparation is exposed to a temperature below the freezing-point of water. At 21° F., the change is effected during the freezing.

The peroxide of iron, which has thus become crystalline, has a much paler colour than the amorphous substance, and is but slightly soluble in acetic acid of spec. grav. 1·030, but readily soluble in acetic acid of spec. grav. 1·0759. If to this solution 8 vols. of water be added, a portion of the iron separates in a few days as a reddish-yellow deposit.

Wittstein has further tested these statements. The hydrated oxide employed in the experiment was analysed, and had the composition $Fe^2 O^3, 3HO$.

After this had been frozen in the pasty state during a night at a temperature of 17° F., and the mass had become quite solid, the hydrate appeared distinctly crystalline under the microscope. It had then the following composition on analysis:—

Oxide of iron..... 10·46
Water ..... 3·60 } , representing $Fe^2 O^3, 3HO$,

and consequently the same quantity of water as before it was frozen.

Wittstein then tested this frozen oxide in its behaviour with tartaric and citric acids. Equal quantities of gelatinous amorphous peroxide were put into three test-tubes, two of which were then exposed for a night to severe frost, and again thawed. Into the tube

which had not been exposed to the frost, containing amorphous hydrate, a couple of crystals of tartaric acid were dropped, and an equal quantity into one of the other tubes; into the third tube the same quantity of citric acid was introduced, and all these tubes were placed in a room in which the temperature during the experiment was from 50° to 61° F., and shaken from time to time. In the first tube complete solution had taken place in the course of half an hour; in the second it required six hours; and in the third nine hours. From this it appears that this frozen hydrate is certainly less soluble in organic acids than the amorphous hydrate, but still more so than that which has become crystalline by long keeping. The cause of this is very probably to be found in the circumstance previously ascertained by Wittstein, that the latter only contains the half of the original water, whilst the frozen hydrate still retains the whole of it.—Wittstein's *Vierteljahrsschrift*, ii. p. 373.

ANALYTICAL CHEMISTRY.

On the Employment of Chlorine in Analysis. By MM. Rivot, Beudant *and* Daguin. *Report by* M. Pelouze.

Chlorine has long been employed in the analysis of mineral substances. Sometimes these substances are exposed at an elevated temperature to the action of a stream of dry gaseous chlorine; sometimes the contact is effected in presence of water.

The former method is applicable to substances the chlorides of which are volatile, such as sulphur, arsenic, tin and antimony, to separate them from non-volatile chlorides, such as those of iron, copper, nickel, cobalt, &c. As however the latter chlorides are not absolutely non-volatile, the separation thus obtained in the dry way is never exact, and can never furnish a precise result, except to a very skilful operator, who has been much accustomed to experiments of this kind.

In the second method of analysis, the chlorine may become an oxidizing agent; it is thus that it peroxidizes iron and cobalt, and converts arsenious acid, dissolved in water acidulated with muriatic acid, into arsenic acid. It will be remembered that upon this property is founded the chlorometric method generally adopted in manufactories, which was invented by Gay-Lussac.

Chlorine then has long been employed in a certain number of analyses, both in the dry and humid way; but the present investigations will infallibly extend its employment.

The authors' experiments all relate to the employment of chlorine in the humid way, sometimes in alkaline, sometimes in acid solutions.

In the former of these conditions, that is, in presence of a free alkali, the oxidizing action is extremely energetic, and generally

causes the substance to attain its highest degree of oxidation; and it may be readily conceived that it may be especially useful in bringing metals or oxides, which furnish acids when combined with oxygen, to the state of soluble salts. These salts are thus separated from those oxides which are insoluble in alkalies.

In the second case, that is to say, in an acid medium, the oxidizing action of the chlorine is much less energetically exhibited; it is only exerted upon a very small number of metals, such as lead and manganese, which pass into the state of binoxides, and become insoluble in the acid.

The following are the principal results attained by the authors:—

I. *Action of Chlorine in Alkaline Solutions.*

Sulphuret of lead is converted into peroxide, which is completely insoluble, and into an alkaline sulphate. Thus the very difficult question of the complete separation of lead and sulphur is resolved, and the analysis of galena effected with equal rapidity and exactitude.

Oxide of lead, dissolved in potash, is converted by chlorine into peroxide, which remains dissolved, forming with the alkali a combination which is soluble in presence of an excess of potash. Thus, under different circumstances, which may be reproduced at pleasure, the peroxide of lead may be separated in a state of purity, and either become free, or remain in solution combined with the alkali.

Hydrated oxide of iron, natural or artificial, is rapidly converted into ferric acid, which, combining with the alkali, gives a solution of a very deep red colour. This fact had already been pointed out by M. Fremy, at the time when he discovered ferric acid. The ferric acid is not formed when the temperature of the alkaline liquid is reduced below 32° F.; nor if the temperature be raised to 104° or 122° F. in presence of quartz and of some other substances which possess the singular faculty, which will shortly be referred to, of modifying the ordinary reactions of chlorine.

When chlorine in an alkaline solution reacts upon sulphuret of iron, the sulphur is dissolved in the state of sulphuric acid, whilst the iron remains insoluble in the state of sesquioxide; and it is only after the complete acidification of the sulphur that the oxide of iron becomes dissolved in its turn, passing into the state of ferric acid.

When an arsenical pyrites, well pounded, is treated in this manner, the sulphur and arsenic are readily obtained in solution in the form of alkaline sulphate and arseniate, and the iron as insoluble peroxide. This state is very easily attained by stopping the action of the chlorine as soon as the liquid begins to acquire colour, and heating it for a few moments with a little pulverized quartz.

The oxides of manganese are pretty quickly converted into alkaline permanganate, if a tolerably concentrated alkaline solution be employed, and at a temperature of 104°–122° F. On the other hand, in operating at a temperature below 32° F., no manganic acid is produced by the action of chlorine. But if the solution be allowed to return to the ordinary temperature in contact with the oxide, the

green manganate of potash is formed. Thus we may obtain at pleasure by the action of chlorine, binoxide of manganese, or an alkaline manganate or permanganate.

Oxide of copper has a great tendency to combine with the fixed alkalies; the compound is soluble, and stable even at the point of ebullition in presence of a great excess of alkali. In the determination of copper, precipitated in the form of oxide by potash, a certain quantity of this compound is always formed. Its presence may however be avoided, at least in great part, by effecting the precipitation in an ammoniacal liquid. It is still better avoided by passing the chlorine into the alkaline fluid, without ammonia, until the alkali is almost completely saturated.

The sulphurous copper minerals, well pulverized, may be easily analysed by the action of chlorine in the presence of an alkaline fluid. The copper and other metals remain insoluble in the form of oxides; whilst the sulphur, arsenic, and antimony dissolve completely, forming alkaline salts. The presence of blende in these minerals is in general inimical to the precision of the reactions.

Oxides of cobalt and nickel, recently precipitated by potash and suspended in an alkaline fluid, pass rapidly to the state of sesquioxides under the influence of a stream of chlorine. In the analysis of minerals of nickel and cobalt, there is generally much difficulty in separating these metals exactly from arsenic and antimony; this difficulty may however be very easily got rid of by operating in the following manner:—

The mineral is dissolved in nitric acid, the solution diluted with water, and a great excess of potash added to it; it is then gently heated, and a stream of chlorine passed into it until the precipitate is quite black. The fluid then contains the arsenic and antimony in the form of alkaline salts; the insoluble portion contains the metals in the state of sesquioxide, and not retaining the least trace of arsenic or antimony.

Phosphoric acid may be separated, like arsenic and antimony, from those metals which form sesquioxides or deutoxides, such as iron, nickel, cobalt and lead.

The determination of free sulphur containing organic matters, such as is employed in such large quantities in the manufacture of sulphuric acid, presents serious difficulties when it is attempted to peroxidize it with nitromuriatic acid, or with nitre in a state of fusion. The employment of chlorine as an oxidizing agent in a hot concentrated alkaline solution always succeeds well. If it be required to determine the sulphur contained in a sample of commercial sulphur, or in a precipitate of sulphuret of arsenic or antimony produced in an analysis, or in natural sulphurets, the sample is heated for some hours in a solution of potash, which dissolves the sulphur and the sulphurets of arsenic or antimony completely. Chlorine is then passed into the liquid, when in a very short time the three substances pass into the state of sulphuric, arsenic and antimonic acids, which remain dissolved as alkaline salts. It is then only necessary to acidify the liquid by muriatic acid, to enable the sul-

phuric acid to be precipitated by chloride of barium, after the excess of chlorine has been driven off by heat.

The sulphate of baryta must be washed for a long time, calcined, and digested in muriatic acid and a little chloride of barium. It is only after a second washing and a second calcination that the weight of the sulphate of baryta can be taken for the calculation of the quantity of sulphur. The necessity for these operations arises from the property possessed by sulphate of barium of carrying down with it a certain quantity of the salts contained in the solution, and only abandoning them by washing after calcination. They are indispensable in the determination of sulphur in the form of sulphate of baryta, whatever be the nature of the oxidizing agent employed.

The action of chlorine in a solution of potash serves for the determination of the sulphur in all metallic sulphurets. For this purpose the sulphuret must be perfectly pulverized, and digested for some hours in a solution of potash heated to 122°–140° F.; the chlorine is then passed in. The sulphur is rapidly oxidized, and dissolves in the form of sulphate of potash, whilst the metals are converted into oxides, and remain insoluble. The sulphuric acid is precipitated from the alkaline liquid when filtered and acidified with muriatic acid, by chloride of barium.

This method is advantageous, especially for the sulphurets which contain lead, because this metal remains insoluble in the state of peroxide. There is no reason to fear the numerous embarrassments usually caused by the slight solubility of sulphate of lead.

A great number of organic substances are directly soluble in potash, or become so by the oxidizing action of chlorine. In the solutions thus obtained, the reactions of mineral analytical chemistry can generally take place in the same manner as in the absence of organic matters. The action of chlorine and alkalies is particularly useful for the removal of the paper of filters, on which the sulphurets of zinc, lead, and some other more or less volatile metals have been collected. The getting rid of the paper by the action of chlorine in an alkaline solution is an advantageous substitute for burning, which almost always causes loss.

One of the substances which present the greatest difficulties is the vulcanized India-rubber, into which oxides of lead and zinc are often introduced. This substance is first of all submitted to the prolonged action of boiling nitric acid, which reduces it into a state of minute division; water and an excess of potash are then added to the turbid liquid, and a current of chlorine is passed into the mixture; the oxides of zinc and lead are deposited, together with a white resinous matter; the sulphur remains dissolved in the form of an alkaline sulphate, and is determined as sulphate of baryta. As to the insoluble portion, it is treated with acetic acid, which dissolves the oxides of zinc and lead, and these are afterwards precipitated as sulphurets by sulphuretted hydrogen.

By this means the exact determination of the mineral substances contained in the caoutchouc may be effected in very little time; and this is certainly an example of one of the most difficult analyses, in consequence of the presence of organic matter.

II. *Action of Chlorine in a Liquid containing Free Acetic Acid and a certain proportion of Alkaline Acetates.*

Under these circumstances chlorine has a much less energetic oxidizing action than in presence of caustic alkalies. Thus free sulphur and the sulphur of metallic sulphurets only become very slowly acidified; the metals, which do not form very permanent peroxides, remain dissolved, or dissolve as protoxides in the free acetic acid. On the other hand, those metals which are capable of forming stable peroxides, undecomposable by acetic acid, give rise to such peroxides, and in this manner may be exactly separated from the other metals.

Lead and manganese are those to which this action is the most readily applicable. They may be separated thus from the alkalies, magnesia, &c., and from several metals, especially zinc, copper, nickel, &c. The operation must be carried on in the following manner:—

An acetic solution of the oxides is prepared, to which a certain quantity of acetate of soda is added, and the whole heated to 122° or 140° F. A current of chlorine is then passed into it, and interrupted as soon as the peroxide is deposited, which soon takes place. This is washed by decantation, and filtered. The insoluble portion contains all the lead or manganese; the liquid, the other oxides.

This process cannot be employed for the separation of lead and manganese from iron and cobalt. In presence of these metals, the precipitation of the binoxide is effected with difficulty, and the precipitate always retains a noticeable proportion of oxides of iron and cobalt.

In concluding this report, we have yet to call the attention of all chemists to a fact mentioned in this memoir, namely, the very singular property possessed by many substances and certain powders otherwise inert, of inducing a rapid evolution of oxygen in alkaline solutions into which chlorine is being passed. This phænomenon resembles the remarkable decomposition of oxygenated water and that of chlorate of potash in contact with the oxides of copper and manganese. It may be produced with facility and certainty by directing a current of chlorine into a solution of potash previously brought to a temperature of 194° or 212° F., and holding in suspension some quartz in fine powder, iron pyrites, arsenical copper, or oxides of copper, nickel and cobalt.

When this decomposition commences, it almost entirely resists the oxidizing action of the chlorine; but it may be prevented, in analytic operations, by reducing the mineral substances of which the composition is to be ascertained, to a very fine powder.

The evolution of oxygen just referred to is sometimes observed during the manufacture of chlorate of potash on a large scale, both when the chlorine passes into the milk of lime at a temperature above 140° F., and when the chlorate of lime is heated with the chloride of potassium.

The presence of silica in the lime is sufficient to explain this evolution of oxygen, and the diminution in the weight of the chlorate of potash which is caused by it.—*Comptes Rendus,* December 5, 1853, p. 835.

THE CHEMICAL GAZETTE.

No. CCLXXII.—February 15, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Upon Anthranilic, Benzamic and Carbanilic Acids.
By Dr. B. W. GERLAND.

THE author has investigated the above-named acids, which have hitherto been regarded as three isomeric acids of the formula $HO, C^{14} H^6 NO^3$, and of which it has also been supposed that they might be identical. He has found that benzamic and anthranilic acids are distinct acids, but that carbanilic acid is identical with benzamic acid.

The anthranilic acid employed in the investigation was prepared according to Liebig's method, the benzamic acid by Zinin's process. The salts of the two acids are very similar.

A very essential distinction, which serves sufficiently to mark the difference between the two acids, was discovered by the author by moderately heating the salts of both series with hydrate of potash. By this means the substances of the anthranilic acid series furnish carbonic acid and aniline very readily; those of benzamic acid, on the contrary, empyreumatic products and no aniline, and consequently ammonia. Aniline is only furnished by the latter when strongly heated.

In order to test further the constitution of the two acids, which the author, following Kolbe, supposes to be

Anthranilic acid. Benzamic acid.

$$HO\left\{\begin{matrix} CO \\ CO^2 \end{matrix}\ \begin{matrix} H \\ C^{12} H^5 \end{matrix}\right\} N \qquad HO\left\{C^{12}\begin{matrix} H^4 \\ H^2 N \end{matrix}\right\} \frown C^2, O^3;$$

both were treated with nitrous acid. Nitrous acid, prepared from arsenious acid and nitric acid, when acting upon a dilute watery solution of anthranilic acid, produces an evolution of nitrogen, unaccompanied by carbonic acid, the fluid remaining perfectly clear. If the introduction of the nitrous acid gas be interrupted as soon as the evolution of the bubbles of nitrogen ceases, and the solution be then concentrated by evaporation, it solidifies on cooling into a reticulated mass of fine, colourless, acicular crystals, which are readily purified by pressing between blotting-paper and recrystallization. The substance thus obtained is salicylic acid. The analysis of the substance, dried at 212° F., gave—

Carbon	60·26	60·38	14	60·87
Hydrogen	4·35	4·20	6	4·35
Oxygen	35·39	35·42	6	34·78

Anthranilic acid is consequently converted by nitrous acid, by the acquisition of oxygen, into nitrogen, water and salicylic acid, HO, $C^{14}H^{6}NO^{3}+NO^{3}=HO, C^{14}H^{5}O^{5}+2N+HO$.

By further treatment of the salicylic acid with nitrous acid, another new acid is obtained; the salicylic acid obtained from the oil of the Gaultheria behaves in the same manner. Benzamic acid, on the other hand, when treated with nitrous acid, furnishes no salicylic acid. A red amorphous precipitate is produced, with evolution of nitrogen gas, free from carbonic acid.

The precipitate when dried presents the appearance of an amorphous scarlet powder. This is insoluble in water and alcohol, but is readily dissolved by fixed alkalies and their carbonates into a red fluid, from which acids again precipitate the substance unchanged. When boiled with water, it cakes together into a resinous mass.

The analyses of this red acid varied in regard to the amount of carbon between 58·0 and 59·8 per cent., and with respect to the amount of hydrogen from 3·9 to 3·4 per cent. The brown precipitates obtained at different times by the precipitation of the neutral ammoniacal salt with nitrate of silver, sulphate of copper or acetate of lead, exhibited still greater differences. Thus the quantity of oxide of silver in the silver salt varied between 42·9 and 51·5 per cent.; the amount of lead contained in the lead salt, between 38 and 49 per cent. Concentrated acids dissolve this substance, depositing it again unchanged on the addition of water.

When nitrous acid acts for a considerable time upon the red substance diffused in water, the latter becomes completely dissolved; and the solution, which has a nauseously-bitter taste, acquires a reddish-brown colour. When this is evaporated to the consistence of a syrup, beautiful yellow crystals of a new acid are deposited; its potash salt is precipitated in golden-yellow scales by alcohol and æther (binitrophenylate of potash?). Fuming nitric acid, when boiled with benzamic acid, converts it into nitropicric acid.

It appears from this that benzamic and anthranilic acids are two distinct acids, possessing the same composition. Both acids furnish with sulphuric and nitric acids peculiar double acids, which crystallize beautifully.

Sulphobenzamic Acid, $2HO.\left\{\begin{matrix}C^{14}H^{6}NO^{3}\\SO^{3}\end{matrix}\right.+2HO$, forms a network of colourless crystals, of a diamond-like lustre. Their solution in water has an intensely sweet taste; when neutralized by solution of potash and evaporated, it furnishes sulphobenzamate of potash. When the acid solution is boiled with carbonate of baryta, insoluble sulphate of baryta and benzamate of baryta are formed, with evolution of carbonic acid. The same decomposition is effected by carbonate of lead, and even chloride of barium, when boiled with the acid solution. Analysis:—

Carbon	42·3	14	41·2
Hydrogen	4·9	10	4·9
Nitrogen.....	6·5	1	6·8
Oxygen	38·0	10	39·2
Sulphur	8·3	1	7·9

Nitrobenzamic Acid, $2HO.\left\{\begin{matrix}C^{14}H^{6}NO^{3}\\NO^{5}\end{matrix}\right.$, forms small scales or shining laminæ, which remain unchanged in the air, and are readily soluble in hot water and alcohol. Their watery solution, when sulphuric acid and protosulphate of iron have been added to it, gives the reaction of nitric acid. Analysis gave,—carbon, 41·7 per cent., and hydrogen, 4·3 per cent. The above formula requires 42·0 per cent. carbon, and 4·0 per cent. hydrogen. With bases it behaves like the preceding acid.

Anthranilic acid furnishes exactly similar compounds; it only differs in this respect from the preceding, that when heated with sulphuric acid, it is decomposed with a violent evolution of carbonic acid.

With regard to the carbanilic acid of Chancel, the author observes, that it appeared probable to him that it is identical with benzamic acid. With Kolbe, he regards benzoic acid as the oxide of the conjugate radical

$$(C^{12}H^{5})\frown C^{2},\ i.e.\ \text{as}\ HO.(C^{12}H^{5})\frown C^{2}O^{3}.$$

Nitrobenzamide therefore

$$=\left(C^{12}\left\{\begin{matrix}H^{4}\\NO^{4}\end{matrix}\right)\frown C^{2},\left\{\begin{matrix}O^{2}\\H^{2}N\end{matrix}\right.;$$

the carbanilamide produced from it by the action of sulphuret of ammonium consequently stands to it in the same relation as benzamic acid to nitrobenzoic acid, and therefore

$$=\left(C^{12}\left\{\begin{matrix}H^{4}\\H^{2}N\end{matrix}\right)\frown C^{2},\left\{\begin{matrix}O^{2}\\H^{2}N\end{matrix}\right.,$$

i.e. a benzamide, $(C^{12}H^{5})\frown C^{2},\left\{\begin{matrix}O^{2}\\H^{2}N\end{matrix}\right.$, in the radical of which 1 equiv. of hydrogen has been replaced by amide. Carbanilamide, consequently, in the first stage of its decomposition by hydrate of potash, must only give off the half of its nitrogen in the form of ammonia:—

Carbanilamide.

$$\left(C^{12}\left\{\begin{matrix}H^{4}\\H^{2}N\end{matrix}\right)\frown C^{2}\left\{\begin{matrix}O^{2}\\H^{2}N\end{matrix}\right.+KO.HO$$

Carbanilate of potash.

$$=KO.\left(C^{12}\left\{\begin{matrix}H^{4}\\H^{2}N\end{matrix}\right)\frown C^{2},O^{3}+H^{3}N.$$

It is evident from this that carbanilic acid is identical with benzamic acid, as may also be seen from the following table:—

Benzoic acid.

$$HO.(C^{12}H^{5})\frown C^{2},O^{3}.$$

Benzoic acid.

$$HO.(C^{12}H^{5})\frown C^{2},O^{3}.$$

Nitrobenzoic acid.

$$HO.\left(C^{12}\left\{\begin{matrix}H^{4}\\NO^{4}\end{matrix}\right)\frown C^{2},O^{3}.\right.$$

Nitrobenzoic acid.

$$HO.\left(C^{12}\left\{\begin{matrix}H^{4}\\NO^{4}\end{matrix}\right)\frown C^{2},O^{3}.\right.$$

Nitrobenzoic æther.

$$C^{4}H^{5}O.\left(C^{12}\left\{\begin{matrix}H^{4}\\NO^{4}\end{matrix}\right)\frown C^{2},O^{3}.\right.$$

Nitrobenzamide.

$$\left(C^{12}\left\{\begin{matrix}H^{4}\\NO^{4}\end{matrix}\right)\frown C^{2},\left\{\begin{matrix}O^{2}\\H^{2}N.\end{matrix}\right.\right.$$

Carbanilamide.

$$\left(C^{12}\left\{\begin{matrix}H^{4}\\H^{2}N\end{matrix}\right)\frown C^{2},\left\{\begin{matrix}O^{2}\\H^{2}N.\end{matrix}\right.\right.$$

Carbanilic acid.

$$HO.\left(C^{12}\left\{\begin{matrix}H^{4}\\H^{2}N\end{matrix}\right)\frown C^{2},O^{3}.\right.$$

Benzamic acid.

$$HO.\left(C^{12}\left\{\begin{matrix}H^{4}\\H^{2}N\end{matrix}\right)\frown C^{2},O^{3}.\right.$$

Ann. der Chem. und Pharm., lxxxvi. p. 143.

On the Isomeric Compounds of Sulphuret of Antimony with Oxide of Antimony. *By* H. Rose.

Compounds of sulphuret of antimony with oxide of antimony are obtained by fusing these substances together in all proportions. They have been known since the earliest periods under the name of *vitrum antimonii.*

If the compound contains little oxide and much sulphuret, and the fused mass be not poured out to form a thin plate, but cooled in a porcelain crucible or small cup, the mass when cool is black and crystalline, with a metallic lustre; the outside is black and glassy, with a metallic adamantine lustre. This may be very distinctly observed by pouring the fused mass in large drops upon porcelain. The lower surfaces of the cooled drops, where they come in immediate contact with the cold porcelain, are glassy; whilst the other portions, which cooled more gradually, are crystalline. The glassy portions give a reddish streak upon unglazed porcelain, whilst the crystalline portions give a black one. The former are perfect non-conductors of electricity, the latter conductors.

If more oxide and less sulphuret be employed, the compound may be obtained crystalline by cooling it extremely slowly. It is then of a grayish-black colour, gives a streak which has a reddish tinge when rubbed upon unglazed porcelain, and is a half-conductor of electricity.

If this compound, when fused, be poured in large drops upon cold porcelain, the outside, which has cooled rapidly, is perfectly glassy and of a reddish colour. The inside is granular and black. The outer portions give a scarlet-red streak on porcelain; the inner, a

black one, with a tinge of red. The former is a perfect non-conductor of electricity, the latter a half-conductor.

Both compounds with much or little oxide may be obtained in a perfectly vitreous state by pouring them when fused into cold water. They are then complete non-conductors of electricity.—*Bericht der Akad. der Wiss. zu Berlin*, 1853, p. 250.

Upon some Compounds of Cadmium. By Dr. E. Schüler.

The author has prepared and investigated the following compounds in Prof. Wöhler's laboratory:—

Crystallized Sulphuret of Cadmium (Artificial Greenockite):—This was obtained by mixing well-dried sulphuret of cadmium with 5 parts of carbonate of potash and the same quantity of sulphur, and exposing the whole for about an hour to a moderate heat. After washing away the sulphuret of potassium, crystals of sulphuret of cadmium were found in the crucible.

Its spec. grav.=4·5 (that of Greenockite is 4·8 according to Breithaupt); its hardness=3·5. With dilute muriatic acid it evolves sulphuretted hydrogen; the acid afterwards produces no further effect at ordinary temperatures. Concentrated muriatic acid produces a violent evolution of the same gas.

Sulphate of Cadmium, exposed to a strong red heat in a stream of hydrogen, does not, like sulphate of zinc, furnish an oxysulphuret, but gives sulphuret of cadmium and metallic cadmium.

Crystallized Oxide of Cadmium is obtained in apparently regular microscopic octahedra, by the ignition of the nitrate.

Ammoniaco-chloride of Cadmium, $CdCl, 3NH^3$.—When the solution of chloride of cadmium is precipitated by ammonia, hydrated oxide is obtained, which, when dissolved in an excess of ammonia, and this saturated with muriatic acid, furnishes the above salt. Potash eliminates ammonia from it. When heated on platina foil, this double compound fuses at rather a low temperature, forming a clear fluid, which on cooling solidifies into a laminar crystalline mass. A portion of the compound is volatilized during the fusion, and the whole of it may be sublimed without residue by continued heat. If it be heated in a glass tube, the phænomena produced are essentially the same. The salt is perfectly anhydrous. Analysis:—

Cd	38·81	1	39·21
Cl	25·06	1	24·94
NH^3	36·13	3	35·85

Sulphite of Oxide of Cadmium and Ammonia, $CdO, SO^2 + NH^4 O SO^2$, is obtained when a solution of chloride of cadmium is supersaturated with ammonia, and sulphurous acid is passed into the clear solution. Analysis:—

Cd	41·87	1	41·56
SO^2	42·05	2	41·89
$NH^4 O$	16·08	1	16·55

Cyanide of Cadmium, CdCy.—The author precipitated this from a solution of chloride of cadmium, as neutral as possible and not too

much diluted, by means of cyanide of potassium. In dilute solutions and in acid fluids no precipitate is produced. It is a pulverulent amorphous mass, which undergoes no change in the air; when heated with access of air, it becomes first brown, and then black, whilst a brown coating of oxide of cadmium is formed. When heated in a glass tube, the compound evolved no water, nor was any oxide of cadmium produced; but a metallic spot of cadmium covered the lower portion of the tube. Muriatic acid dissolves it immediately, with evolution of hydrocyanic acid. Analysis:—

Cd.....	68·1	1	67·870
Cy.....	31·9	1	32·130

Protocyanide of Copper and Cadmium, $2CdCy + Cu^2Cy$.—Hydrocyanic acid is poured over freshly-precipitated hydrated oxide of cadmium; this is dissolved with difficulty. Hydrated carbonate of copper is added until the whole is dissolved. Before complete solution is effected, the portion remaining in the fluid acquires a lavender colour; this is partially soluble in water, leaving oxide of cadmium, while carbonic acid and cyanogen are disengaged. The clear colourless fluid afterwards becomes rose-coloured, and lastly purple-red. From this solution, especially when concentrated, dingy brownish-red crystals are deposited, which are difficult of solution in cold water. When they are dissolved in a little boiling water, a tough, red, viscous, oleaginous mass separates from the clear rose-coloured solution. When left to itself for a considerable time, this substance solidifies into a mass of crystals, which must be recrystallized from boiling water. These possess a remarkable glassy lustre; they are oblique four-sided prisms, belonging to the clinorhombic system. In the air, and at temperatures from 212° to 302° F., they are completely unchanged; at a higher temperature they become opake and dull, without losing their form. If the heat be still further raised, they fuse into a brown fluid, and then a rapid decomposition takes place; the odour of hydrocyanic acid is perceptible; a portion of the cadmium is volatilized, whilst a brown inflated mass remains, which contains copper and cadmium.

Sulphuretted hydrogen throws down sulphuret of cadmium; muriatic acid precipitates protocyanide of copper, with evolution of hydrocyanic acid. The crystals dissolve in concentrated muriatic acid only by the assistance of heat. They are insoluble in ammonia and its salts, and in solution of potash. Chlorine passed over them gives them a green colour. Sulphate of copper gives a green, chloride of iron a brown, and perchloride of mercury a white precipitate, all soluble in an excess of the precipitant. Nitrate of protoxide of cobalt furnishes a brown precipitate. Nitrate of protoxide of mercury gives metallic mercury. Analysis:—

Cd	45·900	45·20	45·45	45·51	2	44·1
Cu	24·399	24·62	24·51	24·51	2	25·0
Cy	29·701	30·18	30·04 ·	29·98	3	30·9

Percyanide of Copper and Cadmium, $2CdCy + CuCy$, is obtained by dissolving the hydrated oxides of the two metals at the same time

in hydrocyanic acid. The colourless solution is evaporated in the air without the employment of heat. It furnishes oblique four-sided prisms, which possess a beautiful lustre. When heated to 212° F., they lose 18·4 per cent. in weight, and fall into a fine powder, which no longer exhibits any traces of crystallization. In this operation, besides a very distinct odour of prussic acid, a considerable deposit of water on the sides of the tube is perceptible. A portion of the cadmium afterwards becomes volatilized, and at last a dark yellowish-brown amorphous substance remains. This salt, like the preceding, is readily decomposed by acids. Both salts possess distinct alkaline properties, and a peculiar metallic taste, which penetrates back into the throat. Analysis:—

Cd ..	49·57	50·08	50·38	50·01	2	50·429
Cu ..	14·05	14·13	14·02	14·07	1	13·872
Cy ..	36·38	35·79	35·60	35·92	3	35·699

Protocyanide of Mercury and Cadmium, 2CdCy+3HgCy, is obtained by the solution of the hydrated oxide of cadmium and oxide of mercury in hydrocyanic acid. It forms white opake crystals, which are permanent in the air. They are right-angled four-sided prisms, with a distinct striation parallel to the principal axis. The crystals contain no water of crystallization; when strongly heated they crackle, and become completely decomposed. During this process all the mercury and a portion of the cadmium are driven off. The salt is readily soluble in cold water; it is completely decomposed by dilute acids. Very concentrated solution of potash separates metallic mercury. Sulphurous acid first produces a slight turbidity in the solution, which is rapidly increased by heat, from the separation of a white, flocculent, voluminous mass. Most of the salts of the oxides of heavy metals produce no precipitate in it. Analysis:—

Cd	19·47	1	20·4
Hg	56·09	1	55·2
Cy	24·44	1	24·4

Lastly, the author acted with cadmium upon iodide of æthyle in a closed tube. He obtained no cadmium-æthyle, but a residue of a basic iodide of cadmium, and a large quantity of a gas, which was perhaps the gas obtained in a similar manner by means of zinc, and regarded by Frankland as isolated æthyle.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 34.

On Aldehyde-ammonia. By Prof. Wöhler.

Colourless crystals of aldehyde-ammonia are not decomposed by concentrated solution of potash. The crystals, as is well known, become brown when exposed to air and light; they also dissolve in the ætherial mixture in which they have been produced, forming a clear brown fluid. When this brown mass was distilled with caustic baryta, a considerable quantity of ammonia and a volatile substance of peculiar odour passed over; the residue consisted of formiate of baryta.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 375.

On the Estimation of Urea, and on a Method for the Determination of this Substance and Chloride of Sodium in the Urine. By Prof. LIEBIG.

[Concluded from page 47.]

Determination of Peroxide of Mercury in a Solution of its Nitrate.

When a solution of phosphate of soda is added to a solution of pernitrate of mercury, a white precipitate of phosphate of mercury is immediately produced; and this, when allowed to stand for some time under the fluid, becomes crystalline. No precipitate is furnished by solution of bichloride of mercury.

If to the first precipitate, whilst still flocculent, a solution of chloride of sodium be added, the salts become changed into bichloride of mercury and phosphate of soda, and the precipitate disappears. From this the author derives the following process for the determination of the peroxide of mercury in a solution of its nitrate. 1 equiv. of phosphate of mercury requires for its resolution 1 equiv. of chloride of sodium; if the quantity of the latter be known, the quantity of the former may be ascertained. The process requires first of all the preparation of a normal solution of chloride of sodium, which is to be effected in the following manner:—

According to their atomic weights, 108 parts of peroxide of mercury require 58·2 chloride of sodium, or 200 parts of peroxide require 108·52 of chloride of sodium.

If 20 cub. centims. of a saturated solution of chloride of sodium be mixed with 566·8 cub. centims. of water, we obtain 586·8 cub. centims. of a dilute solution of the chloride, containing in the whole 6368 milligrms. of chloride of sodium (the quantity contained in 20 cub. centims. of the saturated solution). 10 cub. centims. consequently contain 108·52 milligrms. of chloride of sodium, representing 200 milligrms. of peroxide of mercury; 1 cub. centim. therefore corresponds to 20 milligrms. of the peroxide.

To ascertain with some degree of accuracy by this method the quantity of peroxide of mercury in a nitric solution, this solution must not be concentrated, partly with a view to more accurate measurement, and partly because the limits of the reaction may be more distinctly ascertained in dilute than in concentrated fluids: it answers well when the mercurial solution to be examined contains only from 180 to 200 milligrms. of peroxide of mercury.

For the purpose of ascertaining the degree of concentration, the following preliminary experiment should be instituted:—10 cub. centims. of the solution of chloride of sodium are mixed with 4 cub. centims. of a cold saturated solution of phosphate of soda (the officinal salt); the mercurial solution is then dropped into this until a precipitate, which does not disappear on shaking, is produced. Supposing that 2·4 cub. centims. are required to produce this effect, these represent 200 milligrms. of peroxide; 10 cub. centims. will therefore contain 800 milligrms. of peroxide, and this is too concentrated. Such a solution ought to be diluted with 3 vols. of water before the actual testing.

10 cub. centims. of this diluted mercurial solution are measured into a beaker, and 4 cub. centims. of the above-mentioned solution of phosphate of soda are added to it. The normal solution of chloride of sodium is then allowed to drop into the mixture, the whole being kept in constant motion until the white precipitate is completely redissolved. Towards the end of the experiment the solution of chloride of sodium should be dropped very slowly.

The addition of the solution of chloride of sodium must be made very soon after that of the phosphate of soda; if only a few minutes be allowed to elapse between these operations, the phosphate of mercury becomes crystalline, and is then no longer soluble, or only dissolves with difficulty. Moreover, the mercurial solution must not contain too much free acid; it contains the proper quantity, when after the addition of the phosphate of soda the mixture no longer has an acid reaction. If it possess an acid reaction, a few drops of carbonate of soda must be added, until a basic salt is thrown down; this is again dissolved by the addition of 1 or 2 drops of nitric acid.

As in redissolving the precipitate a few drops too much of the solution of chloride of sodium will perhaps always be added, an error attaches to this method, which will give the quantity of peroxide of mercury a little larger than it really is. As however the phosphate of soda is somewhat soluble in the fluid, and the solution of chloride of sodium itself is valued accordingly, this error is generally very small. On the other hand, if the mercurial solution be dropped into the mixture of phosphate of soda and chloride of sodium, a little too much of the former will always be added, in order to render the precipitate visible, for this never becomes permanent until the fluid is saturated with it.

The determination becomes more exact by proceeding in the following method, which is a combination of the two preceding. 10 cub. centims. of the mercurial solution are measured into a beaker, and 3 or 4 cub. centims. of a solution of phosphate of soda added to it; the solution of chloride of sodium is then immediately dropped in from the burette until the precipitate has disappeared. Supposing that 12·5 cub. centims. of the solution of chloride of sodium have been employed; 12·5 cub. centims. of the same solution are measured off, 3 or 4 cub. centims. of the solution of phosphate of soda are added to them, and the mercurial solution is then dropped into the mixture from the burette, until a precipitate begins to make its appearance. If 10·25 cub. centims. of the mercurial solution be required for this purpose, we have—

I.	10·00	c.c.	mercurial sol.	required	12·5	c.c.	chloride of sodium sol.
II.	10·25	...	...	...	12·5	...	... ...
	20·25	...	...	...	25·0	...	... ...

Now as every cubic centimetre of the solution of chloride of sodium represents 20 milligrms. of oxide of mercury, the 25 cub. centims. of this solution employed indicate 500 milligrms. of peroxide of mercury contained in 20·25 cub. centims of the mercurial solution.

Method of determining Urea in Urine.—The two methods pre-

viously described for the determination of chloride of sodium, and for that of peroxide of mercury in solution in nitric acid, are especially adapted to furnish a new method for the determination of urea, which, yielding to no other in accuracy, and being capable of being rapidly effected, is particularly serviceable for medical purposes. It depends upon the circumstance that pernitrate of mercury precipitates urea.

When a dilute solution of this salt is slowly added to a dilute solution of urea, and the free acid of the mixture is neutralized by baryta-water or diluted solution of carbonate of soda, a white, flocculent, somewhat puffy precipitate, which is insoluble in water, is produced. If the alternate addition of the mercurial solution and carbonate of soda be continued as long as a precipitate is produced, a point is reached at which, on the addition of the latter salt, the spot, where the drop falls, becomes yellow in consequence of the precipitation of basic pernitrate of mercury. At this period all the urea, with the exception perhaps of imponderable quantities, is included in the precipitate, which contains 4 equivs. of peroxide of mercury to 1 equiv. of urea. The precipitation of yellow oxide by the addition of carbonate of soda to the mixture only occurs when a volume of the mercurial solution has been added, in which to 10 parts of urea in the solution there are 77 parts of peroxide of mercury. This however is 4 equivs. of peroxide to 1 equiv. of urea.

If the solution of pernitrate of mercury be added to the solution of urea as long as a precipitate is produced, the mixture, on the addition of carbonate of soda, remains white; if the original mixture remains standing for a time, the precipitate becomes crystalline; it then contains the salt above described with 3 atoms of peroxide of mercury, which crystallizes in six-sided tables, and the clear fluid above the precipitate now furnishes a yellow instead of a white precipitate. A portion of the peroxide of mercury is therefore again dissolved in the acid solution. It is necessary, therefore, in order to ascertain whether the proper quantity of the mercurial salt has been added for the production of the precipitate with 4 equivs. of peroxide of mercury, to neutralize the fluid with carbonate of soda. If a drop of the mixture in a watch-glass remains white on the addition of carbonate of soda, there is still some urea in the solution; but if, on the contrary, a yellowish film is produced, the limit is attained or slightly exceeded. It is clear, therefore, that if the amount of oxide of mercury contained in the solution be known, the quantity of urea contained in the fluid may be readily ascertained from the quantity of the mercurial solution employed in its precipitation. Or if a certain quantity of the mercurial solution be required for the precipitation of a known quantity of urea, the same quantity consumed by a fluid containing an unknown amount of urea will indicate the same quantity of that substance.

The author gives the following process for the preparation of the mercurial solution for the determination of urea. 4 grms. of pure urea are first of all dissolved in water, and diluted to exactly 200 cub. centims. (the solution of 4 grms. of urea in 200 cub. centims.

of water would give 201·75 cub. centims. of fluid, or 1·75 cub. centims. too much). Of the mercurial solution for the determination of the urea in the urine, 20 cub. centims. should be exactly sufficient to indicate the quantity of urea in 10 cub. centims. of the above solution of urea (containing 200 milligrms. of urea); 1 cub. centim. of it will therefore represent 10 milligrms. of urea. The mercurial solution must therefore contain a sufficient quantity of peroxide of mercury to form with 100 milligrms. of urea the nitric acid compound with 4 equivs. of peroxide of mercury, and a slight excess of peroxide of mercury, which serves to indicate the complete precipitation of the urea; so that after the addition of the last drops of the 10 cub. centims. of the mercurial solution to the solution of urea, if a few drops of solution of carbonate of soda be added to a portion of the mixture, a distinct yellow tinge is perceptible. The author has ascertained, by a series of experiments, that for 100 milligrms. of urea, which according to calculation only require 720 milligrms. of peroxide of mercury (in the form of its nitrate), 10 cub. centims. of the mercurial solution must contain 772 milligrms. of peroxide of mercury to produce a distinct reaction for oxide of mercury in dilute solutions. Every cubic centimetre of the mercurial fluid must therefore contain an excess of 5·2 milligrms. of peroxide of mercury. The most simple mode of preparing this test-fluid is by dissolving pure metallic mercury in pure nitric acid in a beaker, and keeping the mixture in a warm place, with frequent additions of nitric acid, until no traces of evolved nitrous acid fumes are to be seen; it is then evaporated to the thickness of a syrup in the same vessel on the water-bath; and, lastly, diluted with so much water that the dilute fluid may contain exactly 7·140 grms. of mercury in 100 cub. centims. This is done by diluting the fluid in which 100 grms. of mercury have been dissolved, until the volume of the whole amounts to 1400 cub. centims.

If the solution of the pernitrate of mercury be prepared from crystallized nitrate of the protoxide, the quantity of peroxide of mercury in the solution must be ascertained either in the usual manner, or by the process above described. Before making use of the solution, its correctness is to be tested by means of a solution of urea of known strength, such as that just mentioned, containing 200 milligrms. of urea in 10 cub. centims. It is as well not to dilute the concentrated mercurial solution to the required strength at once, but to employ somewhat less water, then to test it with the solution of urea, and complete the dilution afterwards.

When the test-fluid is valued to a solution of urea containing 2 per cent. of that substance, 15 cub. centims. of the latter solution will require 30 cub. centims. of the mercurial solution for the precipitation of the urea and the indication of its completion; in this manner 45 cub. centims. of a mixture are obtained, containing 30 times 5·2=156 milligrms. of free peroxide of mercury; every cubic centimetre consequently contains 3·47 milligrms. of the peroxide. When the solution of urea contains 4 per cent. of urea,

60 cub. centims. of the mercurial solution are required for 15 cub. centims. of it; so that 75 cub. centims. of a mixture are obtained, containing 312 milligrms. of free peroxide of mercury, or 4·16 milligrms. in every cubic centimetre, and consequently 0·69 milligrm. more than is necessary to produce the original colour.

The experiments have shown that in analyses of urine in which the quantity of urea is increased, an error is produced which gives the amount of urea as too small. In the case just supposed, for instance, instead of 60 cub. centims., only 59·37 cub. centims. of the mercurial solution would be added. This error is avoided by adding to the mixture, when 15 cub. centims. of urine have taken more than 30 cub. centims. of the mercurial solution, half the additional number of cubic centimetres of water, before testing with carbonate of soda. For instance, if 20 cub. centims. be required in addition, 10 cub. centims. of water are to be added. It is then always found that a few drops more of the mercurial solution must be added.

For the same reasons, when the quantity of urea in the urine is only 1 per cent., instead of 15, 15·3 cub. centims. of the mercurial solution must be added; to do away with this error, which increases the amount of urea, 0·1 cub. centim. must be deducted from the entire quantity employed for every 5 cub. centims. less than 30. Thus if 25 cub. centims. of the mercurial solution be required for 15 cub. centims. of urine, the quantity of urea, 249 milligrms., is expressed by 24·9 cub. centims. of the solution, and so forth.

For the determination of the urea in urine, a mixture of 2 vols. of baryta-water with 1 vol. of a cold saturated solution of nitrate of baryta is first prepared; 1 vol. of this fluid is then mixed with 2 vols. of urine. For this purpose a small glass cylinder, of any desired size, may be employed; this is twice filled to overflowing with urine, and covered each time with a glass plate, so as to expel the excess. The same cylinder is then once filled in the same manner with the barytic solution, and its contents poured with the urine into a beaker, when a precipitate is produced, which is to be filtered off. For each analysis, 15 cub. centims. of the filtered fluid, corresponding to 10 cub. centims. of urine, are to be employed.

To this volume of urine, without previous neutralization, the standard mercurial solution is dropped from a burette, the whole being kept constantly stirred; when no further precipitation is observable, the testing is to be commenced. For this purpose a few drops of the fluid with the precipitate are poured from the beaker into a watch-glass; a few drops of solution of carbonate of soda are then allowed to run down from the edge of the watch-glass: this is best effected from a caoutchouc pipette. If the mixture still retains its white colour after a few minutes, the addition of the mercurial solution must be continued until a fresh sample taken from the beaker gives a distinct yellow colour on the addition of the carbonate of soda. The number of cubic centimetres of the mercurial solution is then ascertained, and corrected according to the quantity of urea in the urine in the manner already described.

Process for the Determination of Urea in Urine containing Chloride of Sodium.

When the quantity of chloride of sodium in the urine amounts to 1 or 1½ per cent., it has an influence upon the determination of urea by means of nitrate of mercury. When to 10 cub. centims. of a pure solution of urea, 20 cub. centims. of the standard mercurial solution are added, the addition of carbonate of soda to this mixture produces a distinct coloration of precipitated oxide of mercury. If 100 or 200 milligrms. of chloride of sodium be added to the mixture, and it be tested afresh, the yellow colour is not produced on the addition of the carbonate of soda; and in order to reproduce this, 1½–2½ cub. centims. more of the mercurial solution must be added; the indicated quantity of urea is consequently too much by 15–25 milligrms., and the same occurs with urine.

The author here gives some results, and observes that he has ascertained these facts by a great number of observations.

For their explanation he refers to the decomposition of chloride of sodium by means of nitrate of mercury. A solution of urea containing chloride of sodium can be precipitated by nitraet of oxide of mercury only when the chlorine of the chloride has produced its corresponding quantity of bichloride of mercury; and in a solution of 200 milligrms. of urea and 100 milligrms. of chloride of sodium in 10 cub. centims. of water to which 20 cub. centims. of the mercurial solution are added, the excess of the mercurial salt, which should have given the yellow colour on the addition of carbonate of soda, does not exist in the form of nitrate, but in that of bichloride; the change in the indication arises therefore from the formation and presence of the bichloride. Instead of 3·46 milligrms. of peroxide of mercury in the form of nitrate, the mixture contains the corresponding quantity of mercury in the form of bichloride.

If a solution of bichloride of mercury be diluted with water until carbonate of soda produces a brownish-yellow precipitate of oxychloride of mercury and then a drop of nitric acid be added to it, and the carbonate of soda dropped in, no precipitate is produced, or at the utmost a whitish turbidity makes its appearance, which after a considerable time deposits single brownish-yellow laminæ. It is in the same way that the excess of bichloride of mercury is contained in the mixture of the mercurial solution with that of urea, the nitric acid of the former being principally contained in it in a free state. This converts a portion of the carbonate of soda into bicarbonate, which does not precipitate the bichloride of mercury. If a mixture contains a larger quantity of chloride of sodium, the carbonic acid set free may not be sufficient to prevent the precipitation of all peroxide of mercury; the brownish-yellow precipitate then makes its appearance.

The experiments show that with urine which contains from 1 to 1½ per cent. of chloride of sodium, 2 cub. centims. must be deducted in order to obtain the correct number of milligrammes contained in 10 cub. centims. And when the quantity of chloride of sodium contained in various urines differs even to a greater degree

than this, the results are still comparable one with another, as the error only affects the absolute quantity of urea, so as to produce an inaccuracy of 15 to 20 milligrms. in 10 cub. centims. of urine.

Consequently, when the absolute quantity of urea in a urine is to be determined, the chlorine must be removed, and the chloride of sodium converted into nitrate of soda by means of nitrate of silver in the following manner:—A solution containing 11·601 grms. of fused nitrate of silver is diluted with water to 400 cub. centims.; 1 cub. centim. contains then 29·01 milligrms. of nitrate of silver, and represents 10 milligrms. of chloride of sodium. When containing this quantity, this solution corresponds with the mercurial solution described at page 44 of the last Number; the same quantity of each serves to indicate the same quantity of chloride of sodium; and if 12·5 cub. centims. of the latter must be added to 10 cub. centims. of urine to produce turbidity, 12·5 cub. centims. of the silver solution must also exactly precipitate the chlorine.

In conclusion, the author observes that these methods have already been confirmed by a great number of experiments, which have been performed by Vogel and Bischoff.—*Ann. der Chem. und Pharm.*, lxxxv. p. 289.

On the supposed Volatilization of Phosphoric Acid.
By R. Fresenius.

Bunce has stated that acid fluids containing phosphoric acid undergo a considerable loss of that acid during evaporation. Fresenius has ascertained by experiment that this supposition arises from an error. He has also found, that at the temperature of 302° F., often employed in drying, and perhaps also at lower temperatures, the tribasic phosphoric acid in many salts is converted into the bibasic acid. Precipitation in the usual way by magnesia and ammonia produces a non-crystalline but somewhat flocculent precipitate, and a portion is dissolved in the water. Hence the loss.

The author then examined into the change that takes place when phosphate of soda is evaporated to dryness with an excess of muriatic acid. 4·1775 grms. of crystallized phosphate of soda were dried on the water-bath with an excess of muriatic acid, and the residue put into a small cup was dried for several hours at 302° F. until it no longer underwent any loss of weight. It weighed 1·9890 grm., and consisted of $PO^5\,NaO, HO + NaCl$:—

Na	27·00	2 =	46·0	27·14	per cent.
PO^5	41·67	1	71·0	41·88	...
Cl	21·02	1	35·5	20·95	...
O	4·67	1	8·0	4·72	...
HO.....	5·64	1	9·0	5·31	...

The residue, dried at 302° F., consequently consists of 1 equiv. of acid pyrophosphate of soda and 1 equiv. of chloride of sodium (PO^5, $2NaO, HO + ClH = PO^5, NaO, HO + NaCl + HO$).

Moreover, even when the above-mentioned precipitate, after drying at 302° F., is brought to a strong red heat so as to drive off

muriatic acid and water, no phosphoric acid is volatilized. The examination of a residue treated in this manner showed that it consisted of 1 equiv. of pyrophosphate of soda, 1 equiv. of metaphosphate of soda and 1 equiv. of chloride of sodium. The change undergone by the residue, dried at 302° F., when heated to redness, is consequently as follows:—

$$2(PO^5, NaO, HO + NaCl) = PO^5, 2NaO + PO^5, NaO + NaCl + ClH + HO.$$

Ann. der Chem. und Pharm., lxxxvi. p. 216.

On the Constituents of Linaria cymbalaria. *By* M. Walz.

The distillate of the plant contains a fat, which the author separated from the watery portions by means of æther. After the spontaneous evaporation of the æther there remained a fatty mass of scale-like crystals, which, when heated and rubbed between the fingers, emitted a peculiar odour. The acid watery distillate was neutralized with caustic baryta, and evaporated to dryness in the vapour-bath. The saline mass obtained was of a brown colour, and only partially soluble in water, leaving a brown tasteless mass. The soluble portion was decolorized as far as possible by pure charcoal, and evaporated to a crystallizable state. This mass contained acetic acid in combination with another acid. The remaining vegetable mass was then repeatedly extracted with water; half the extract, which was rather bitter and had an acid reaction, was rapidly evaporated on the water-bath to the consistence of an extract, and then treated with alcohol of spec. grav. 0·833; to the other half neutral acetate of lead was added as long as any precipitate was formed. When this had been well washed, half of it was decomposed by sulphuretted hydrogen and the other half by sulphuric acid. The filtrate from the latter operation had a dark brown turbidity, and could only be slowly filtered, from the adhesive resin being suspended in the fluid. In the clear filtrate there existed, in addition to some resin, a brown colouring matter, which is readily soluble in water; a tannin, striking a green colour with salts of iron; the inorganic acids; and lastly, tartaric and malic acids.

The same constituents were found in that portion of the lead precipitate which was decomposed by sulphuretted hydrogen.

In the fluid filtered from the lead precipitate, only a small precipitate was furnished by basic acetate of lead. After filtration from this precipitate, the solution only contains a bitter principle, to which the author gives the name of *cymbalarine*. This was precipitated by means of tannic acid from the fluid after it had been freed from lead by carbonate of soda; the precipitate was digested in alcohol, which acquired a deep golden-yellow colour; the digestion was repeated as long as the alcohol dissolved anything, and then the whole of the extracts were digested with pure oxide of lead until all the tannic acid was combined with the oxide. The greater part of the alcohol was then carefully distilled off, and the remainder got

rid of by spontaneous evaporation: in this manner a yellowish-brown scaly residue, which changed readily into an amorphous resinous mass, was obtained; it had a very bitter disagreeable taste, and was only partially soluble in water.

The entire residue was digested with æther, which soon acquired a yellow colour, and left on evaporation a dark golden-yellow resinous mass, of a very sharp disagreeable taste. This is soluble in absolute alcohol, and must be regarded as the cause of the pungency of the plant. The portion which was insoluble in æther is the bitter principle of the plant, not however quite in a pure state; when exposed to the air it becomes moist, and when burnt leaves a little alkaline ash. For this reason it was again dissolved in water, and precipitated by pure tannin; the entire white precipitate soon collected into a resinous mass. This was washed as much as possible with water, then carefully dried, reduced to a fine powder, mixed with alcohol and pure oxide of lead, and put in a warm place. After the tannin had combined with the oxide of lead, the tincture was filtered, the alcohol partially distilled off, and the remainder left to evaporate spontaneously. White scales were soon formed on the surface, which continued increasing, and in time gathered together into a mass, and dried into a yellowish-white powder. In this state it is the cymbalarine of the author.

The ashes of the plant had the following composition:—

Potash	4·93
Soda	4·62
Lime	24·00
Magnesia	7·92
Phosphoric acid	11·91
Sulphuric acid	2·78
Muriatic acid	2·63
Carbonic acid	12·36
Silica	5·46
Charcoal and sand	23·39

The *Linaria cymbalaria* therefore contains—

Acetic acid,
Peculiar fatty acid,
Tannic acid,
Tartaric acid,
Malic acid,
Phosphoric acid,
Sulphuric acid,
Muriatic acid,
Silica,
Bitter principle (cymbalarine),
Pungent resin (cymbalacrine),
Resin,
Odorous principle (cymbalaros-[mine),
Chlorophylle,
Colouring matter,
Humine substances,
Gum,
Mucus,
Potash,
Soda,
Lime,
Magnesia,
Oxide of iron (traces).

Journ. für Prakt. Pharm., xxvii. p. 129.

ANALYTICAL CHEMISTRY.

New Process for ascertaining the Presence of Iodine and determining its Quantity. *By* M. DE LUCA.

THE following process for the determination of iodine was indicated to the author by M. Balard, and employed by him in the examination of two samples of bromine which were supposed to contain iodine. The process is very simple, and its sensibility is almost unlimited; it will succeed even in the most inexperienced hands, and the presence of chlorine and bromine does not interfere in the least.

The liquid, supposed to contain iodine in the form of an iodide, is introduced into a tube closed at one end, and a few drops of sulphuret of carbon or chloroform added to it; a very dilute watery solution of bromine is then added. The bromine only decomposes the iodides, without touching chlorides or bromides; the mixture is shaken; the free iodine dissolves in the sulphuret of carbon, to which it gives a violet colour of greater or less intensity, or a rose colour if it be in very minute quantity.

In this manner the iodine contained in $\frac{1}{100}$dth milligrm. of iodide of potassium may readily be discovered, and with some care this sensibility might even be raised to $\frac{1}{1000}$dth milligrm.

The employment of an excess of bromine must be avoided, as this would form with the iodine a compound which does not furnish the violet tinge with the sulphuret of carbon; and, moreover, an excess of bromine gives a yellow colour to the sulphuret of carbon.

If the solution of the iodide be alkaline, it must be neutralized with weak nitric acid before submitting it to the treatment just described.

This process may also be applied to the quantitative determination of iodine. For this purpose a normal solution of bromine is first prepared from 1 grm. of bromine and 4 litres of distilled water; 4 cub. centims. of this solution will then contain 1 milligrm. of bromine. To 40 cub. centims. of this solution, containing 10 milligrms. of bromine, sufficient water is added to make the quantity up to 1 litre, that is to say, 960 cub. centims. of distilled water; each cubic centimetre of this new solution will contain $\frac{1}{100}$dth milligrm. of bromine.

Two slender graduated pipettes are required for the operation,—one for the solution of bromine, the other for the sulphuret of carbon; for it is necessary always to employ the same quantity of sulphuret of carbon, in order to appreciate the shade of colour in the same quantity of fluid. After a first operation the sulphuret of carbon coloured by the iodine is removed, and replaced by a fresh addition of this fluid; and this is repeated until the sulphuret no longer acquires any colour.

This mode of determination may be compared to that of silver by means of chloride of sodium, in which the treatment is stopped as

soon as the addition of the chloride no longer produces a precipitate; in this case the action is stopped when the sulphuret of carbon ceases to acquire colour.

The quantity of bromine employed, less that which produced no colour in the sulphuret of carbon, indicates by a simple calculation the quantity of iodine set at liberty and contained in the substance under analysis. The normal solution of bromine should be added by drops, and the number of drops contained in a cubic centimetre must be previously ascertained.

By this process the quantities of chlorine, bromine and iodine contained in a given mixture may be determined simultaneously in the following manner:—By means of solution of silver of known strength, the quantity of silver required to precipitate the three metalloids is ascertained; then, by means of bromine, the quantity of iodine is determined; lastly, by means of chlorine, the bromine and iodine are determined together, and the necessary elements of calculation are obtained.

The solution of chlorine employed in the determination of the bromine and iodine is prepared as follows:—A solution of chlorine in distilled water is first made, and then diluted with water to a certain volume. The value of the solution thus prepared is determined by means of a solution of iodide of potassium of known strength, treated as above with sulphuret of carbon. The quantity of chlorine employed to expel all the iodine from the iodide of potassium indicates the value of the solution. The solution of chlorine should be recently prepared, and kept in a blue bottle with a ground-glass stopper. When it has been prepared some days, it is advisable to ascertain its strength before making use of it.—*Comptes Rendus*, Dec. 5, 1853, p. 866.

On the Red Colour produced with Quinine and Ferrocyanide of Potassium. *By* A. Vogel.

This red coloration, which, according to an observation of the author's already published, may be employed as a test for sulphate of quinine, sometimes fails (Fresenius). The author now gives the following process, by which the coloration is produced with certainty. Sulphate of quinine is put into a test-tube, and water poured over it, but so that a great portion of the crystals remain undissolved. Of this fluid, which is to be kept shaken to keep the sulphate of quinine in suspension, a few drops are poured into a watch-glass, and a sufficient quantity of solution of chlorine added to it to produce a clear fluid of a somewhat yellowish colour. To this chlorinated solution of quinine finely-powdered ferrocyanide of potassium is then added, until it acquires a pale rose-red colour. The pale red colour soon passes to deep red, and with especial rapidity when a little more powdered ferrocyanide of potassium is added.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 122.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Use of the Sulpho-purpuric Acid, or Red Sulphate of Indigo, in the Dyeing of Worsted and Silk. *By* EDWARD HÆFFELY, Ph.Dr., *Member of the Industrial Society of Mulhouse, France, Chemist at Mount Sion Print Works, near Manchester*.*

I TAKE the liberty of drawing your attention to a new fact, demonstrated in the successful application on worsted and silk of the red sulphate of indigo (the phenicine of Mr. Walter Crum).

This chemical compound is produced by the action of sulphuric acid upon indigo, and by throwing the mixture thus obtained into a large quantity of water a few minutes after the contact.

By this means a red-coloured precipitate is formed, which, when well and thoroughly washed on a filter, represents the red compound in question, a very different production from the blue sulphate of indigo in its composition, properties, and as regards the shades produced by it.

I have been able to produce with this red sulphate of indigo shades superior in all respects to those obtained by the employment of the ordinary indigo extract, imitating the prussian blue, and likewise purple shades bearing a resemblance to those produced by the use of logwood and cudbear, which shades, I should observe, cannot be obtained from the commercial indigo carmine (or extract).

Patterns dyed with this red extract of indigo have been highly approved by the judges appointed by the "Société Industrielle de Mulhouse," who gave the preference to the blue and purple colours obtained by the use of this red compound, which dye material has been introduced into commerce, and is actually applied in several dyeing establishments of the neighbouring county of York.

I will now enter into a few details respecting the chemical nature of these two sulphates.

Upon an examination of the formulæ of the two bodies referred to, it will be found that the blue indigo extract is, properly speaking, a hyposulphate of dehydrogenized indigo,—

$$S^2 O^5 + N C^{16} H^4 O^2$$

(the formula of indigo being $N C^{16} H^5 O^2$); whilst the red compound is a sulphate of indigo,—

$$SO^3, HO + N C^{16} H^5 O^2.$$

Upon a comparison of these two formulæ, it will be remarked, that in the case of the blue indigo extract, the indigo and the sulphuric acid have undergone remarkable alterations; the indigo having lost a portion of its hydrogen, and the sulphuric acid a portion of its oxygen, and these two elements, hydrogen and oxygen, having united to form water. But in the case of the red sulphate, the indigo and the sulphuric acid have entered into combination *without* undergoing any change.

As in the composition of this red sulphate the colouring matter

* Communicated by the Author.

is, or appears unaltered, I was induced to entertain the supposition, that it might be beneficially used in dyeing, for the purpose of obtaining fast blue directly,—an operation which might probably replace with advantage the process of obtaining fast blues from vats.

A circumstance which is in favour of the possibility of fixing this indigo on fabrics in a state of indigotine is, that some organic substances (such as sulphovinic acid, sulphoglyceric acid, and other sulpho-acids) possess the property of being decomposed and resolving themselves into their *primitive constituents* by a simple ebullition in water. This red sulphate of indigo may be ranked in that type of organic bodies, where it figures under the name of sulpho-purpuric acid. As it ought to partake in every respect of all the properties of the series of compounds mentioned, it should necessarily, on its ebullition in water, decompose into *free indigo* on one side, and into *free sulphuric acid* on the other. Consequently I presumed that by introducing fabrics into the vessel where the process was going on, and at the moment of the separation of the colouring matter, I could fix this colour upon the fabrics so introduced. But the first experiment I made, with the view of proving the practicability of the supposition, did not turn out to be satisfactory as regards the dyeing of cotton, whilst the worsted and silk took off and successfully retained the colouring matter.

I made three consecutive trials on the occasion,—the first in a neutral bath, the second in an acid bath, and the third in an alkaline one; but in all the three attempts, so far *as the cotton* was concerned, the result was not successful. Hence it appears that cotton has no affinity for this indigo. But silk and worsted may be effectually dyed in the way I have indicated, if the bath be only kept a little acid; I prefer the use of a few drops of muriatic acid. As I have already observed, some of the patterns imitate the prussian blue; and those washed in soap or alkaline water resemble the purple produced from logwood and cudbear, which shades could not up to the present time be produced by the employment of indigo alone.

A question which it will now be worth while particularly to inquire into is this,—whether the blue appears on these fabrics as indigotine or as sulpho-purpuric acid, or as a modification of the one or the other.

I incline very much to the opinion that it is a modification of the indigotine, or of the sulpho-purpuric acid itself; for I found that the sulpho-purpuric acid, in contradiction to the opinion generally entertained, is an *intense red* compound, and not an intense blue one, when dried. Nevertheless, upon examining the patterns dyed with this *red* compound, it is found that they *are blue*, and *not red*; and those washed with alkaline water *are purple*, an effect which is not produced by *indigotine*.

I have not yet been able to solve this question, and for the present only call attention to the new shades obtained by the employment of sulpho-purpuric acid, viz. the *indigo-blue*, resembling prussian blue; and the *indigo-purple*, similar to the shades obtained by the use of logwood or cudbear.

THE CHEMICAL GAZETTE.

No. CCLXXIII.—March 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on the Arsenæthyles. *By* H. LANDOLT.

KAKODYLE, $C^4 H^6 As$, has been regarded as a compound of 1 atom of arsenic with 2 atoms of methyle; it was therefore interesting to ascertain whether a corresponding compound of æthyle could be formed directly by the combination of arsenic and æthyle. The investigation not only confirmed this supposition, but has also brought to light two other radicals, corresponding with stibæthyle, $SbAe^3$, and stibmethylium, $SbMe^4$. The new compounds are consequently as follows:—

1. $As(C^4 H^5)^2$ = arsenbiæthyle.
2. $As(C^4 H^5)^3$ = arsentriæthyle.
3. $As(C^4 H^5)^4$ = arsenæthylium.

The object of the present memoir is only to establish the existence of these three radicals, and to characterize them with reference to their combining proportions. A complete review of the combinations of the arsenæthyles will only be possible when the investigations have been carried still further.

The materials required for the preparation of the arsenæthyles are iodide of æthyle and arseniuret of sodium. The former is obtained in the usual manner by dissolving iodine in alcohol, putting the solution into a retort with some phosphorus, and heating it until the fusion of the latter, and then shaking the fluid until it is decolorized. It is then poured into another retort, a fresh portion of iodine dissolved in it, and then returned upon the phosphorus. This operation is repeated until the fluid fumes strongly; for this purpose the alcohol requires twice its weight of iodine. The entire operation must be rapidly performed; from 1 lb. to $1\frac{1}{2}$ lb. of iodine may easily be brought into combination in an hour. If the fluid becomes too hot, the retort is to be cooled with cold water. When the action is completed, the whole is left standing for twelve hours, when the greater part of the iodide of æthyle separates; it is then distilled off from the same retort on the water-bath. The iodide of æthyle obtained usually contains a small quantity of phosphorous acid; it consequently takes up a little more iodine, without becoming coloured; when completely saturated, it is shaken and distilled with water, and the distillate rectified over chloride of calcium. In this manner a quantity of iodide of æthyle is obtained equal in weight

to the iodine employed; a portion of iodine is always lost by the formation of hydriodic acid and the volatilization of iodide of æthyle during the operation. From 1 to 1½ lb. of iodine was generally employed for the preparation.

The arseniuret of sodium can only be obtained directly; a number of attempts at preparing it in other ways all gave unsatisfactory results. Perfectly pure metallic arsenic is finely divided; dust may be prevented by moistening with alcohol. The dry powder is put into a porcelain crucible with a cover, and the whole enclosed in a larger Hessian crucible, which must also be capable of being well closed. This is then put into a furnace with a good draught, and slightly heated; as soon as arsenical vapours make their appearance, the coals are to be drawn away, the crucibles opened, and some pieces of sodium of the size of peas thrown into the arsenic, when combination immediately takes place, with considerable production of fire. When this is ended, more sodium is added, and the whole is stirred with an iron rod; this is continued until the mass begins to become fluid. For this purpose 1 part of arsenic requires about 1 part of sodium. The action is frequently so violent, that portions of the alloy are thrown out in a state of combustion; the crucible must consequently be covered immediately after the addition of sodium; it is also very advisable to use the pieces of sodium with the naphtha in which they have been kept still adhering to them; the combustion of the naphtha almost completely excludes the air. The access of air must be avoided, and the whole operation should be performed as quickly as possible, as otherwise a considerable portion of the alloy burns away, producing a thick smoke of arsenious acid. When the action is completed, the mass is allowed to cool gradually; the crucible is then broken, and the alloy in fragments put into well-stoppered bottles, which are afterwards filled with quartz-sand; in this manner the alloy may be kept for a considerable time. The broken surfaces exhibit a crystalline texture and a silver-white colour; but when exposed to the air, they soon oxidize and become gray. A portion of the mass is frequently quite amorphous, and presents a liver-brown colour; these pieces however exactly resemble the metallic portions in their other properties, and may consequently also be employed. Arseniuret of sodium is brittle, and may readily be powdered. If it be put into water, a lively evolution of arseniuretted hydrogen gas is produced; this effect is also produced in moist air; it is necessary therefore to use great caution in experimenting with it. The consideration of the composition of the arseniuret of sodium will be entertained hereafter; it cannot be determined by synthesis, as even though the constituents be previously weighed, it very often happens that all the arsenic does not enter into combination, or that a portion of the sodium is dissipated by combustion. The author can therefore furnish nothing positive with regard to the influence which the composition of the arseniuret of sodium may exercise upon that of the arsenæthyles.

With respect to the analysis of the following arseniuretted organic compounds, the author states in general that the determination of

the carbon and hydrogen was effected in the usual manner by combustion with oxide of copper, with which a little chlorate of potash had been mixed. This was effected with most of the substances, without any particular difficulties; slight explosions, which sometimes occurred within the combustion-tube, had no effect upon it. The anterior portion of the tube was always occupied with copper turnings, for the purpose of retaining the excess of oxygen, and in the combustion of the iodine compounds, also the iodine.

Very considerable difficulties stood in the way of the determination of the arsenic. Concentrated nitric acid only produced a very imperfect oxidation of the compounds, so that no result could be obtained in this way. The substance was then burnt with pure oxide of zinc, exactly as in an elementary analysis; the anterior portion of the long combustion-tube, to which a bulb-apparatus filled with water was attached for the regulation of the operation, being allowed to project some inches from the furnace. When the combustion was completed, the contents of the tube were treated with dilute muriatic acid, in which the oxide of zinc was dissolved, whilst the metallic arsenic remained behind with the coal. This arsenic, as well as that which adhered to the walls of the combustion-tube in the form of metallic spots, was dissolved by heating with nitromuriatic acid, and then precipitated from the entire solution by means of sulphuretted hydrogen. The sulphur in the sulphuret of arsenic, collected on a weighed filter, could then be estimated in the usual manner, or the arsenic may be precipitated in the form of arseniate of ammonia and magnesia. In this way the determination of the arsenic was effected several times; but in spite of the greatest care, these determinations sometimes exhibited considerable diversity. This was caused by the circumstance, that in passing the sulphuretted hydrogen through the common solution of zinc and arsenic, in which the latter existed in very small quantity compared with the zinc, some sulphuret of zinc was thrown down with the sulphuret of arsenic, causing the quantity of the latter metal to appear too high.

After several fruitless endeavours to estimate the arsenic in other ways, the author finally adopted the method employed by Löwig and Schweizer for the determination of the antimony in stibæthyle. The compound was introduced into the hinder portion of an ordinary combustion-tube, which was afterwards completely filled with quartz-sand; the vapours of the compound were then passed through the quartz-sand, which was previously brought to a red heat. The decomposition was always completely effected, and the arsenic deposited in metallic spots. The pieces of the tube to which the arsenic was attached, together with the quartz-sand, were then treated with nitromuriatic acid; this was effected in a suitable vessel, adapted to prevent the volatilization of chloride of arsenic, and the arsenic was then precipitated from the solution as arseniate of ammonia and magnesia. This method gave the best results, and the author intends employing it for the determination of the arsenic in some of the following compounds.

The determination of the iodine in those iodine compounds which are only soluble in alcohol was effected by means of nitrate of silver, dissolved in a little water acidulated with nitric acid, and then mixed with a large quantity of alcohol. The iodide of silver was washed first with water, and afterwards with alcohol. The iodine was also precipitated several times by a solution of palladium.

Preparation of the Arsenæthyles.—Two different methods were employed in the preparation of the arsenæthyles. Arseniuret of sodium, mixed with quartz-sand, was put into small retorts, and iodide of æthyle added to it; at the conclusion of the action, the mass was either submitted to dry distillation in the same manner as in the preparation of stibæthyle and stibmethyle, or extracted with æther, by which the organic arsenic compounds were dissolved. The latter method was first employed by Löwig in the preparation of the stannæthyles. The following is a fuller statement of these two methods, and of the products obtained by them.

First Method.—A number of small retorts, to contain about 3 oz. each, and with their necks as short as possible, are to be got ready. These are about two-thirds filled with a mixture of finely-powdered arseniuret of sodium and quartz-sand, and then well corked. The pounding of the alloy is attended with unpleasant effects, as it immediately evolves arseniuretted hydrogen gas in considerable quantity when in contact with the air; it must therefore be powdered as rapidly as possible. The arseniuret of sodium cannot be powdered by itself, as in this case an explosion very soon takes place; but if a little sand be added at the commencement, this does not occur; 4 or 5 parts of fine quartz-sand may be added to 1 part of the alloy. When a retort is charged, a quantity of iodide of æthyle is poured in sufficient to moisten the mass thoroughly; the retort is then attached to the distillation-tube of the apparatus described by Löwig and Schweizer for the preparation of stibæthyle*; this is to be previously filled with carbonic acid gas. Two small flasks are placed in the glass cylinder of this apparatus, and the lower extremity of the distillation-tube is inserted into one of them. The mass in the retort becomes so strongly heated, that a great portion of the iodide of æthyle is immediately distilled off; when the action is completed, more iodide of æthyle is added, and this is repeated as long as any action takes place. These subsequent additions must not be omitted, for although a great excess of iodide of æthyle may be added at first, after the completion of the action a large quantity of undecomposed arseniuret of sodium will be found, with a very small production of arsenæthyle. The last remains of iodide of æthyle are expelled from the retort by a gentle heat. On the application of a stronger heat, arsenæthyle distils over; the lid of the glass cylinder with the tubes is then to be raised, and the tubes turned round until the distillation-tube arrives over the second flask, into which it is to be inserted. The moment when the flasks should be changed is readily known; as soon as the arsenæthyle comes over, the distillation-tube becomes cold, and the drops are formed at its commencement,

* Chem. Gaz., vol. viii. pp. 201, 372.

whilst during the distillation of the iodide of æthyle this portion of the tube appears perfectly dry and feels hot. The heat should be gradually increased to a red heat; when nothing more is coming over, the retort is removed, and a new one put in its place. In each preparation, from twelve to fifteen retorts were usually employed; for these 1 lb. of iodide of æthyle was required, of which the half was regained unchanged; the quantity of arsenæthyle obtained was 2 oz. At the close of the operation the first flask contains iodide of æthyle mixed with some arsenæthyle; the second, a nearly colourless fluid, which however is frequently mixed with a red substance. This fluid is heavier than water, and possesses an insupportable odour, which is strongly provocative of tears; in the air it fumes very strongly at first, and then takes fire, with evolution of fumes of arsenious acid; the ignition takes place most readily when a strip of filtering-paper is moistened with it. This crude product is a mixture of arsenbiæthyle and arsentriæthyle. Its analysis gave 38·38 per cent. of carbon and 8·48 per cent. of hydrogen.

As arsentriæthyle is more volatile than arsenbiæthyle, the readiest method of separating the two radicals is by fractional distillation. The crude product is put into a small retort in an atmosphere of carbonic acid; the retort is then connected with the distillation-tube of the above-mentioned apparatus, the glass cylinder of which is to contain several small flasks, which may be brought under the mouth of the distillation-tube by turning the cylinder round. The retort must be furnished with a thermometer reaching to 482° F.; it is heated by means of a small sand-bath, and during the operation a strong current of carbonic acid is allowed to pass through the apparatus.

For this fractional distillation 2 oz. of the crude product were employed, and the substances passing over collected in five portions. The first portion, coming over between 140° and 281° F., still contained iodide of æthyle; it solidified after some time into crystals containing iodine. The second portion, collected at 284° F., also contained iodine. The analysis of these portions gave—

	I.	II.
Carbon	42·91	42·51
Hydrogen	9·63	9·87

The third fraction, with a boiling-point of 284°–302° F., and the fourth, of 302°–365° F., were pure arsentriæthyle; their analysis gave—

As	..	..	..	..	..	..	1	= 75	46·30
C	44·03	43·61	43·38	43·26	43·22	43·21	12	72	44·44
H	9·41	9·71	9·44	9·52	9·88	9·88	15	15	9·26

Its formula is $As(C^4H^5)^3 = AsAe^3$.

The fifth portion, with a boiling-point from 365°–392° F., gave—

Carbon.....	39·91
Hydrogen	8·89

It was a mixture of arsentriæthyle with arsenbiæthyle; the

colourless, strong, fuming fluid, which remained in the retort with some metallic arsenic, appeared to be nearly pure arsenbiæthyle. This was dissolved in æther, and an ætherial solution of iodine added to it as long as the fluid became colourless, and the æther then distilled off. The residue was a yellow oily substance, of an insupportable odour, which mixed readily with alcohol and æther, but was insoluble in water. Its alcoholic solution, when mixed with a strong solution of nitrate of silver to which alcohol had been added, immediately furnished a precipitate of iodide of silver. This iodine compound was washed with a little alcohol, and then dried over chloride of calcium. Analysis :—

Arsenic	..	..	..	..	1 =	75	28·85
Carbon	18·90	19·30	19·34	19·59	8	48	18·46
Hydrogen ..	4·13	4·45	4·23	4·73	10	10	3·84
Iodine	48·95	48·45	49·13	49·13	1	127	48·85

The formula of this compound is consequently

$$As(C^4 H^5)^2 + I = AsAe^2 I.$$

As has already been stated, crystals containing iodine were formed in the first portion. The same crystals were also produced in the iodide of æthyle, which came over first of all in the preparation of the arsenæthyles, and in particularly large quantities when the portions of arsentriæthyle which first came over were collected in the same flask. In this case the entire fluid often solidified in a few days in acicular crystals. These could be readily separated from the adherent iodide of æthyle by solution in water, and obtained pure by pressing between paper and recrystallization from water or alcohol.

These crystals appeared to be iodide of arsenæthylium $= As(C^4H^5)^4 + I = AsAe^4 I$, for their analysis gave—

Arsenic	..	..	..	..	1 =	75	23·58
Carbon	28·96	28·58	..	..	16	96	30·19
Hydrogen ..	6·97	6·71	..	..	20	20	6·29
Iodine	39·51	39·29	38·75	38·64	1	127	39·94

The formation of this substance takes place exactly like that of iodide of stibmethylium, 1 atom of arsentriæthyle combining with 1 atom of iodide of æthyle.

The method just described of preparing arsentriæthyle and arsenbiæthyle by the dry distillation of the mass, produced by the treatment of arseniuret of sodium with iodide of æthyle, appears to be a very advantageous one ; the radicals can be obtained in considerable quantities in a proportionately short time, and they are readily separated by fractional distillation. The arsentriæthyle is produced in particularly large quantities, and this method is consequently well adapted for its preparation ; the quantity of arsenbiæthyle is always much less, and this radical is frequently not quite pure ; it may always be obtained much more readily by the second method, which will now be described.

Second Method.—The organic arsenic compounds, formed by the

action of iodide of æthyle upon arseniuret of sodium, may also be separated from the rest of the mass by extracting them with æther. This method is especially applicable to the preparation of arsenbiæthyle; iodide of arsenæthylium is also formed as a subordinate product. The arseniuret of sodium is treated with an excess of iodide of æthyle; the mass is extracted with æther on the completion of the action and the ætherial extract, which contains arsenbiæthyle, arsentriæthyle and iodide of æthyle, mixed with absolute alcohol, and then deprived of its æther by distillation. If water be added to the alcoholic fluid, arsenbiæthyle is thrown down, and iodide of arsenæthylium, which is produced by the combination of iodide of æthyle with arsentriæthyle, remains in solution, and may be obtained by evaporation. If in the treatment of the arseniuret of sodium with iodide of æthyle all excess of the latter be avoided, a mixture of arsenbiæthyle and arsentriæthyle is at last obtained; and these two radicals can only be separated by fractional distillation.

The exact process is as follows:—As in the former method, small glass retorts are filled with a mixture of arseniuret of sodium and sand, which is then wetted with iodide of æthyle, and strongly shaken; the retorts are then immediately united with a small receiver by a narrow tube bent downwards. The action soon begins, and iodide of æthyle distills over; this is often coloured by a small quantity of a red pulverulent body. After the cooling of the retort the distillate is poured back into it, some fresh iodide of æthyle added, and the distillation-tube immediately attached again; this must always be done very quickly, in order to exclude the air as much as possible. If on the addition of a third or fourth portion of iodide of æthyle there is no longer any increased production of heat, the retort is to be closed and left to cool. If a great excess of iodide of æthyle has been added, it may be distilled off; this must however not be completely effected for the reason already given, but only carried so far as to leave the mass in the retort still moist. When this operation is carried on with 10 or 12 retorts, their contents are to be put as quickly as possible into a flask containing $1\frac{1}{2}$–2 lbs. of æther, which is then closed (a cover of vulcanized India-rubber is the best closure), and strongly shaken. The flask must be previously filled with carbonic acid. It is then allowed to stand until the supernatant fluid has become clear, when it is poured off into another well-stopped vessel, which is also to be previously filled with carbonic acid. During this decantation the clear yellowish fluid usually becomes somewhat turbid, from the formation of a sulphur-yellow powder, and this makes its appearance in so much the greater quantity the longer the fluid has been in contact with the air. The residue in the flask is again extracted with fresh quantities of æther as long as a portion of the extract becomes turbid when exposed to the air; all these ætherial extracts are then mixed, and put into a retort. A little anhydrous alcohol is then added, and the æther rapidly distilled off in the water-bath. The yellow powder which is formed in the fluid by contact with the

air, cakes together during the distillation, forming a red resinous body, which fuses at about 158° F., and is insoluble in all solvents.

The alcoholic fluid remaining in the retort, which possesses an extremely unpleasant odour, and fumes strongly when exposed to the air, is now transferred into a well-stopped glass cylinder in an atmosphere of carbonic acid, and then mixed with water free from air until a strong turbidity begins to show itself. If the fluid again becomes clear, after a short time it is to be poured away from the oleaginous body which has separated, into a second vessel, in which a considerable quantity of water is added to it, by which arsenbiæthyle is completely thrown down in the form of an oily fluid, of a pale greenish-yellow colour, and a penetrating odour, strongly provocative of tears. This is transferred into a small bottle; the supernatant fluid is then removed by means of a pipette, and kept covered with a stratum of air-free water. In all these operations care must be taken to exclude the air completely; for the slightest access of air immediately causes the formation of a red powder, which mingles with the radical, and renders its purification very difficult. The author will return to the consideration of this red powder. The oily fluid, which was thrown down from the alcoholic solution by the first addition of water, contained the following quantities of carbon and hydrogen:—

Carbon	27·30
Hydrogen	6·08

On the second addition of water, the arsenbiæthyle is obtained pure. The radical, prepared in the above way, and dried upon chloride of calcium, gave the following results on analysis:—

Arsenic	56·92	56·92	56·92	1	= 75	56·39
Carbon	35·87	35·71	35·62	8	48	36·09
Hydrogen	7·72	7·67	7·85	10	10	7·52

Formula, $As(C^4H^5)^2 = AsAe^2$.

Iodide of arsenæthylium is contained in the water which has been employed for the precipitation of the radical; with this there are some other compounds containing arsenic, which however are difficult to separate from one another. A great number of analyses undertaken with these substances has as yet led to no result. If the watery fluid be shaken with æther, a portion of these compounds is dissolved, together with a considerable quantity of iodide of arsenæthylium, although the latter is not otherwise very readily soluble in æther; and if this fluid be then evaporated in the air, it leaves a yellow syrup, of an unpleasant odour, from which the iodide of arsenæthylium separates after some time in fine columnar crystals. It may be separated from the other fluid compounds by treatment with a small quantity of water, and obtained pure by repeated crystallization from water.

Some determinations of the iodine in the iodide of arsenæthylium obtained in this manner were performed in the volumetric way by means of a standard solution of chloride of palladium, of which

1 cub. centim. represented 2·033 milligrms. of iodine. The quantities found were 39·83, 40·19, 39·55, 39·85; the quantity, calculated from the formula $As(C^4H^5)^4+I=39·94$.

If the water employed for the precipitation of the arsenbiæthyle be evaporated on the water-bath, after it has been treated with æther in the manner just described, a small quantity of iodide of arsenæthylium is also obtained. It is however very much contaminated with other oleaginous bodies of a disagreeable odour, and also containing iodine, from which it can only be imperfectly separated.

The mass in the retort in which the arseniuret of sodium was treated with iodide of æthyle, and which, as above stated, was put into a flask, is not wholly exhausted by extraction with æther. If anhydrous alcohol be poured over the residue, fresh quantities of the arsenious organic compounds are dissolved; when the fluid is evaporated, they remain partly in a solid, partly in an oleaginous form. In spite of the utmost care, no pure compounds could be obtained from this residue; but if the entire mass be put into a retort, and submitted to dry distillation with uninterrupted access of air, there passes over, together with a watery fluid, a considerable quantity of an oily body, of a very unpleasant odour, and insoluble in water. If this oily substance, which is usually of a yellowish colour, be allowed to stand for a few days, it separates into two strata; the lower contains iodine, and is very thick; the upper, which is in larger volume, contains no iodine, and is more mobile. This upper stratum is removed, shaken with a little water, and then dried over chloride of calcium. In this manner a clear pale yellowish fluid, of an unpleasant odour, strongly provocative of tears, is obtained; it is insoluble in water, but mixes readily with alcohol and æther. The elementary analysis of this compound gave the following results:—

As	43·17	43·17	43·17	43·17	43·17	43·17	1	=75	42·13
C	40·38	40·25	39·91	39·81	39·65	39·58	12	72	40·45
H	8·92	9·29	9·14	8·90	9·08	8·73	15	15	8·43
O	..	..	..	..	..	..	2	16	8·99

This fluid consequently is the oxide of arsentriæthyle $=As(C^4H^5)^3O^2$, and represents the oxide of stibæthyle $=SbAe^3O^2$.

[To be continued.]

On Phosphuret of Manganese. *By* Prof. Wöhler.

Phosphuret of manganese is obtained in the form of a well-fused regulus, of an iron-gray colour, brittle, permanent in the air, and very crystalline, and of spec. grav. 5·951, by mixing intimately 10 parts of pure calcined oxide of manganese, 10 parts of white burnt bones, 5 parts of white quartz-sand, and 3 parts of calcined lamp-black, and exposing the mixture in a luted Hessian crucible for about an hour to a heat sufficient to melt cast iron in a strong blast-furnace.

The phosphuret of manganese thus obtained is a mixture; the

analysis of a sample gave manganese 82, and phosphorus 18. Muriatic acid left 65·5 per cent. undissolved; the solution contained 24 per cent. of manganese, and during the solution no hydrogen gas capable of spontaneous combustion was evolved. It is consequently a mixture of $Mn^3 P$ and $Mn^7 P$. The quantity of the insoluble residue varied in different experiments.

A similar mixture was obtained by mixing 10 parts of calcined protophosphate of manganese with 3 parts of calcined lamp-black and 2 parts of calcined borax, and exposing the mixture in a charcoal crucible to the heat of a blast-furnace.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 373.

On the Action of Tellurium upon the living Organism. *By* K. Hansen.

The experiments were made upon dogs, partly with tellurous acid and partly with tellurite of potash.

I. Into the stomach of a middle-sized dog, 0·3 grm. of acid tellurite of potash, dissolved in a few drops of solution of potash, were injected. The action immediately took place; the dog lost his vivacity, appeared stupified, and laid himself down quietly. In a minute his breath had acquired an unpleasant garlic-like odour. Vomiting commenced in twenty minutes, and was frequently repeated during the first hour; the appetite was quite lost. On the following day the animal had recovered, but still retained a strong garlic-like smell of tellurium. After he had eaten something, 0·3 grm. of the salt was again given to him. The stupefaction and vomiting took place as on the preceding day. Both the vomit and the excrements were slimy and of a black colour. Under the microscope it was evident that this coloration was due to the presence of minute black points, which underwent no change by the addition of alkalies, sulphuret of ammonium or muriatic acid, but were quickly dissolved when heated with nitric acid. In the afternoon of the same day a third portion of 0·3 grm. was given to the same dog with the same result, making in all 0·9 grm., or more than 14 grains. In three days the dog had perfectly recovered, but still retained a strong smell of tellurium.

II. In a second experiment, 0·5 grm. of tellurous acid were given to a middle-sized dog, and the same quantity again on the following day. The acid was given to him with a piece of meat. The only signs of action were that the breath acquired a slight odour of tellurium, and that the excrements were a little blackened on the second day.

On the third day, 0·7 grm. of acid tellurite of potash in solution were given to the same dog. The vomiting, and other phænomena produced in the first case, now recurred. On the fourth day, 0·7 grm. more were introduced into the stomach of the same dog. In half an hour vomiting commenced, with a discharge of thick mucus from the mouth. On the seventh day, 0·5 grm. of the salt in solution were injected into the jugular vein of the same dog. Convulsions,

with expulsion of fæcal matter, were produced, and death followed in four minutes. The abdomen was immediately opened, when the garlic-like odour was very distinct. In the abdominal cavity there was half a tablespoonful of a clear serous exudation, but no signs of any hyperæmia or inflammation. The stomach and intestines contained some bile, but were otherwise empty; they exhibited no structural change. Their walls were of a blue-black colour throughout, the coloration diminishing in intensity from the mucous to the serous coat. The liver was somewhat darker than usual on its surface, with a tinge of gray, but without any inflammatory spots; the spleen was apparently normal; but the kidneys were of a blue-black colour throughout their substance, as well as all the glands, even the parotid. The walls of the bladder were bluish; the right ventricle of the heart and the veins were filled with blood; the lungs, brain, and spinal cord exhibited the normal appearances. The serum of the blood was not violet. The black colour of the stomach, intestine, kidneys, and glands appeared under the microscope to be due to the deposition of black points, which behaved with reagents in the manner already described. The urine had an acid reaction and a distinct odour of tellurium.

A cataract had been produced in both eyes; the eyeballs were taken out, and when opened gave a distinct odour of tellurium. On the anterior surface of the crystalline lens, a chalk-white mass had been deposited, which had a granular appearance under the microscope. The urine, stomach, liver and intestines, separately examined, were all found to contain tellurium.

In a third and fourth experiment, when tellurite of potash was given to dogs, the results were essentially the same as in the first case.

The author himself afterwards took acid tellurite of potash dissolved by means of potash, thus forming the neutral salt, every day for seven days, an hour before dinner. For the first four days he took 0·04 grm. (more than $\frac{1}{2}$ gr.); the two following days, 0·05 grm. (nearly 1 gr.); and on the last day, 0·08 grm. (or more than 1 gr.). On the first two days drowsiness was produced, but it did not occur in the further progress of the experiment. After the seventh day a feeling of oppression prevailed in the cardiac region, with a tendency to vomiting (which however did not take place), and an unusually plentiful secretion of saliva; the tongue had a whitish coat, and was somewhat swelled, so that the impressions of the teeth were strongly marked on its edges. The appetite was lost. These gastric phænomena did not entirely cease for fourteen days. The most remarkable phænomenon was the garlic-like odour which was acquired by the breath. This made its appearance within a minute of the taking of the first dose of the salt, and was still observable for several weeks. Twenty-four hours after the conclusion of the experiment, no tellurium was to be found in the urine. This experiment has been repeated by Von Röder, with similar results.

A circumstance observed by Prof. Wöhler, but now first published, gives confirmation to this. He noticed that when he was occupied with the investigation of tellurœthyle, his breath had a

garlic-like odour for several weeks; and he perceived the same odour twice in a very high degree in the nocturnal sweats produced by a cold.

Hence the conclusion may be drawn, that the black coloration of the contents of the stomach, intestines, &c., arises from reduced tellurium. From the colouring of the intestines, which is strongest in the mucous coat and gradually diminishes in the serous, a direct absorption of the tellurium separated in the contents of the intestines may be inferred. Simultaneously with the reduction of the tellurium, the formation of a volatile compound also takes place, which is eliminated by the lungs and through the skin.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 208.

On the Fat of Cantharides. *By* Dr. Gössmann.

The fat employed in the author's investigation was collected by Trommsdorff of Erfurt as a subordinate product in the preparation of cantharidine; it was the residue of the distillation of the ætherial extract. The mass was never heated above 95° F.

The fat has an acid reaction and the consistence of butter; it is somewhat granular, very green, and has the odour of cantharides. The water in which it has been washed has a bitter taste, a yellowish colour and an acid reaction. The melting-point of the purified fat is 93° F.; it solidifies again at 90° F.

The fat was saponified with dilute solution of soda; the ley was distilled with sulphuric acid, and the soap decomposed by tartaric acid; thus the fat was examined for volatile and non-volatile acids. The investigation showed that the fat of cantharides consists of acid margarate and oleate of oxide of lipyle.

The analysis of the baryta salt, prepared from the oleic acid of cantharides, gave—

Carbon	61·34	36 =	2700·00	61·79
Hydrogen	9·41	33	412·59	9·44
Oxygen	7·59	3	300·00	6·87
Baryta	21·66	1	956·88	21·90
Oleate of baryta	100·00		4369·38	100·00

The analysis of the margaric acid of the same fat gave—

	Found.	Varrentrapp's analyses.			Calculated.
Carbon	75·55	75·35	75·87	75·66	75·602
Hydrogen ..	12·35	12·33	12·22	12·69	12·560
Oxygen	12·10	12·32	11·91	11·65	11·838

At the instigation of Prof. Heintz, the author afterwards attempted the resolution of the margaric acid into stearic and palmitic acids, and succeeded in separating the latter acid.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 317, and lxxxix. p. 123.

On the Sulphate of the Peroxide of Mercury. *By* H. Eissfeldt.

When this salt is prepared by the solution of mercury in an excess of acid, and driving off the excess of the acid by heat until a

sample exposed to the air no longer becomes moist, the salt is obtained in the form of a powder. If a small quantity of this powder be spread upon a flat watch-glass, and water be poured over it in sufficient quantity to cover it, it becomes first of all perfectly yellow; in a short time, a little more than an hour, distinct crystals are formed in this powder; and in the course of a longer time the whole becomes converted into crystals, sometimes several lines in length, and presenting the appearance of colourless, transparent, square columns. Frequently these crystals enclose some basic salt, when they appear yellow. It depends principally upon the quantity of water added whether white or yellow crystals are obtained; the smaller this is, so much the more certain is the formation of white crystals; the larger the quantity, if not too large, the better formed are the crystals, although always yellow.

The author separated the white crystals from the yellow; they cannot be washed with water without decomposition, for which reason they must be freed from adherent moisture by blotting-paper, and allowed to dry in the air. From analysis, this salt is $HgO, SO^3 + HO$. Dried at 212° F., it gave—

Oxide of mercury.....	72·82	1	72·99
Sulphuric acid.....	27·28	1	27·01

The author then endeavoured to prepare the acid salt, which should remain in solution in the preparation of the basic sulphate. Laminar crystals, arranged in a stellate form and of a silvery lustre, were obtained; these could not be freed from adherent moisture by washing with water without decomposition, and must consequently be dried by means of blotting-paper constantly changed. When dried at 212°, the salt suffers a slight loss. Analysis:—

				Calculated.
Oxide of mercury	71·98	70·51	1	72·99
Sulphuric acid	29·33	28·45	1	27·01

At 212° F. the salt lost 2·08 per cent. As a little excess of sulphuric acid was found in both analyses, it must be supposed that the crystals include some sulphuric acid, which cannot be got rid of by the above-mentioned way, and that this causes the slight loss of water at 212° F. From this it appears that crystals of neutral persulphate of mercury are obtained from an acid solution. It was however by no means impossible that an acid salt might be obtained in another way.

To arrive at some certainty on this subject, neutral sulphate of mercury was dissolved in an excess of sulphuric acid, and the solution evaporated to crystallization. A salt exactly similar to the preceding in appearance was obtained, and its analysis gave the following results. That used in I. was dried *in vacuo*, that in II. at 212° F.:—

	I.	II.		Calculated.
Oxide of mercury	71·95	72·89	1	72·99
Sulphuric acid.....	27·23	27·43	1	27·01

At 212° F. the salt lost 2·31 and 2·77 per cent. of water.

In this case also it appears from the numbers obtained that the salt is anhydrous neutral sulphate of mercury, as the loss of water must be attributed to the hygroscopic qualities of the sulphuric acid, which cannot be completely got rid of.

It appears consequently—

1. That there is a hydrated, crystallizable, neutral sulphate of mercury, composed according to the formula $SO^3\,HgO + Aq$, which can only be obtained from neutral sulphate of mercury by the addition of water in the manner above described.

2. That a crystallizable acid sulphate of mercury could not be prepared, and that consequently the supposition formerly entertained, that this acid salt separates from the acid solution formed during the preparation of the basic sulphate when this is evaporated, is erroneous.—*Archiv der Pharm.*, lxxvi. p. 16.

ANALYTICAL CHEMISTRY.

Improved Apparatus for the Analysis of Coal, and for Organic Analysis generally. *By* J. H. Alexander *and* Campbell Morfit*.

Early in October last, having to make an ultimate analysis of divers specimens of coal, anthracite and bituminous, we had abundant opportunity of observing the want of certainty and uniformity of result in the methods ordinarily recommended and practised for such analysis. With all these methods, where the aim is to induce the organic or other substance under analysis to give off its carbon by combustion, in glass tubes, with oxide of copper, chromate of lead or chlorate of potash, either separately or mixed; and where the effects arise under a simple play of affinities at a high temperature, and are unaided by any external force of mechanical agency, variations occur to such an extent as, in the case of anthracite coal especially, to leave the results, from several assays of the same sample, rarely identical. We have found these variations to depend, among other things, upon the grade of comminution of the matter for analysis, and its mode of intermixture with the oxidizing agents. If, for instance, the coal is too finely divided, it either protects or is protected by the reagents against the effect of the heat, although this may be so high as to fuse the tube and part of its contents. If, on the other hand, the coal be not finely divided enough, it protects itself. We all know the extreme difficulty of driving off the carbon from an anthracite coal, for example, even in an open crucible and over a blast, where sometimes three hours and more are spent in reducing so small a quantity as 1 grm. to ashes; and as for the

* Communicated by the Authors.

mode of intermixture which shall be most favourable for the exposure and contact of the greatest amount of surface between the material and reagent respectively, it is easy to see that, even after having been studied and attained in one instance, its repetition must be more the gift of good fortune than the result of any regular and unfailing manipulation.

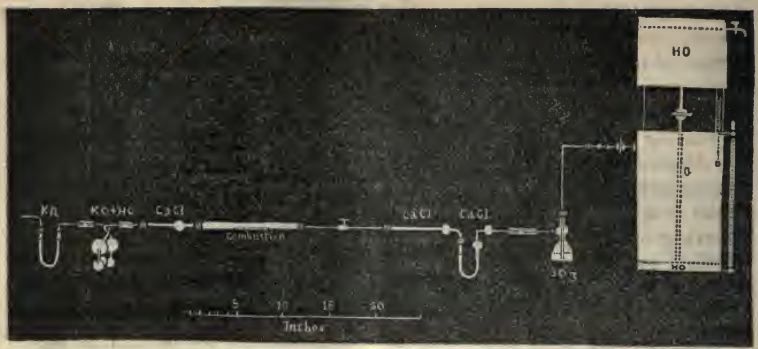
Again, in the ordinary methods, with whatever reagent, the heat necessary to be applied, and the apparatus for its application, prevent in a great degree, if not entirely, the experimenter from observing what is going on in the tube; so that he is left without any optical grounds, or indeed any grounds at all, beyond the cessation of bubbles in the potash bulbs and an inference from the lapse of time, for judging whether the operation is properly complete or not.

Finally, in any of these methods, the ashes of the matter being lost among the fragments of the reagents, there is rendered necessary, for the determination of this item, a partitioning of the original sample and a second special operation under all the scope for differences—slight, perhaps, but yet differences—which such partitioning always implies.

It was under these impressions, and with the view of remedying to some extent the defects which have been noticed, that we came to arrange and use the apparatus of which this note is intended to give the description. We have found in its employment that both from the comparatively low temperature necessary, and from the mechanical mode of applying, and, when requisite, urging the reagent, the rate of the whole process comes under the strictest and most delicate control; that its progress is all the time distinctly seen, and can be judged of; and that the elements usually sought for in organic analysis (and especially in coals, for the purpose of ascertaining their probable heating power) are obtained from one and the same weighed portion.

Other advantages which we find it to possess—such as its convenience, being always ready after having been once arranged; its permanence, being not at all liable to get out of order with ordinary precaution; its œconomy, both as to the time of the experimenter and the money for combustion-tubes, which, in the former modes, answer but for one experiment and are then thrown away, while in this, the tube, except from some extraneous accident, never breaks, and answers for the hundredth experiment as well as for the first; and, finally, the quiet and composure of the whole process, undisturbed by any explosion or decrepitation—need not be dwelt on here. They, of course, will recommend themselves to the practical analyst, and are to be duly appreciated; but are not, in our opinion, to be spoken of in the same category with the main feature of accuracy and reliability of result.

The accompanying cut exhibits in section as much of the arrangement as appears necessary to its being clearly understood in connexion with the description following. The letters there are the chemical symbols to denote the occurrence and position of the several reagents employed.



On the right hand is seen a reservoir of oxygen, somewhat modified from the ordinary Pepys's gasometer. In this, the water-reservoir above is furnished with an outlet and cock (which during use are left open, in order to maintain a constant level), and is fed from another vessel of water, communicating with it in any convenient manner. We use a siphon. The water-reservoir is supported as usual by three stems; only one of them, as shown, is opened and widened to hold a thermometer with a small range and open scale, whose bulb plunges into the oxygen-reservoir below, and serves to indicate the temperature of the gas. The water is allowed to pass into the lower reservoir of gas by a pipe and stop-cock, as usual; and the orifice of said pipe is also made to receive adjutages of varying bore, so as to regulate with considerable exactitude the rate of supply. Connected with the gas-reservoir is a glass tube, which usually indicates the level the water may have attained, and consequently the quantity of oxygen on hand; but in this instance it is intended to answer a more precise quantitative determination. On the tube are inscribed two scales; one, deduced from the known capacity of the gasometer and calibre of the tube, to show at once the number of cubic inches occupied by the water between any two stand-points on the scale, and, of course, when corrected for pressure and temperature, the corresponding volume of oxygen introduced or expelled; and the other, to show at any epoch the fraction of inches of mercury corresponding to the actual pressure of the water, counted downwards from the constant level in the upper reservoir (the design of which constancy is now apparent) to its stand in the tube; which fraction is convenient to be added at once to the observed barometric pressure, in order to give the total pressure under which the oxygen is delivered. With this total pressure and the observed temperature, the normal volume of oxygen used from epoch to epoch can be readily ascertained; the purpose of which ascertainment is, as will be seen presently, to have a check upon the numerical results otherwise obtained. This method of registering the quantity of oxygen used is not perhaps the best that could be devised, and leaves something to be desired on

the score of minute measurement. But it was the most convenient application to the apparatus that we possessed; and as it can be read, with a vernier, to about one-tenth of a cubic inch (or $\frac{1}{300}$th of a grain in weight nearly), it is probably commensurate with the accuracy usually thought sufficient in checking a result furnished by other means.

With the stopcock outlet in the upper part of the oxygen-reservoir, as seen on the left of the gasometer, is connected by a pierced cork, one end of a right-angled tube that plunges its other end into a flask of strong sulphuric acid, through which the oxygen, as delivered, passes and parts with its moisture. The remainder of the moisture is supposed to be absorbed by the chloride of calcium contained in the next two tubes, as shown; the first of which, a double-bulbed U-tube, is connected by a caoutchouc wrapper with the branch proceeding from the upper tubulure of the sulphuric acid flask, and the small end of the second is bent at right angles, and is corked into the open end of the first. There is no particular virtue in these various bends and tubulures; they were used because the pieces happened to be at hand, and possessed, as we judged, the quality of containing a sufficient extent of chloride of calcium in a short linear space.

If our judgement as to this sufficiency is correct, the oxygen passes quite dry into the next small tube, furnished with a stopcock, and connecting the last chloride of calcium tube with the combustion-tube itself.

This tube is needlessly long for the purposes it has to answer, which are in fact met by the stopcock; but it happened to be on hand, and we did not desire to cut it. The purposes intended are threefold,—1st, by shutting off the cock while the gasometer is open and oxygen is being delivered, to secure a sufficient residence of the oxygen in the chloride of calcium tubes for this gas to become dry, in fact, to secure a store of dry oxygen; 2nd, by a similar shutting off, to convert the combustion-tube into a tube closed at one end, and thus allow of any incidental moisture being drawn off with an exhausting syringe in the usual way; and 3rd, by shutting off more or less, to regulate the flow of dry oxygen, or, if necessary, to cut off the supply altogether. When the experimenter has no assistant, the use of this stopcock for regulation is more handy than the one on the gasometer; for the second purpose, we have never used it ourselves, preferring to dry the combustion-tube and its contents by a sustained current of oxygen under pressure, from which there is no danger of vitiation to the result by introducing carbonic acid, as is always the case when a current of atmospheric air is employed in the same way; the first purpose is almost always advantageous, and in some cases indispensable.

We have now come to the combustion-tube, which is a piece of hard German white glass, open at both ends for receiving corks. This is lined for about one-third of its length in the middle with a helix of clean and bright copper wire, the purpose of which is to reduce any of the oxides of nitrogen that might be generated from

the matter in combustion, and thus to secure the transmission of this element in a free state through the remaining channels of the apparatus. It will, of course, be generally proper to clean and renew the surface of this helix by any convenient method after each experiment. Resting on this helix is a platinum scroll of known weight, holding the matter for analysis, and retaining its ashes for being weighed after the combustion is completed. This combustion we have always so far effected with hand-lamps of alcohol, having Argand burners, the heat given by which is quite high enough to ensure in a few minutes the oxidation, in this atmosphere of oxygen, of all the carbon contained in a half grain, or even a grain of coal. To assist in the rapidity of oxidation, we found it advantageous to spread the mass of pulverized matter as thinly as possible over the surface of the platinum scroll. Instead however of these Argand burners, whose small extent renders the scintillating and perfectly-oxidizing temperature too local, we propose to employ hereafter a lamp with oblong hollow wicks, extending over nearly the entire length of the combustion-tube, and separated by metallic diaphragms of sufficient height to prevent the spontaneous communication of flame from one to the other, so that each wick may be lighted successively, as desired. This lighting should be commenced and the heat applied first at the end of the combustion-tube nearest the gasometer, on account of the great density of the carbonic acid produced, to assist in the discharge of which we have found it proper to give the whole apparatus from the gasometer onward an inclination downwards of about half an inch per foot.

The gaseous products of combustion pass off first into a chloride of calcium tube, whose smaller end is corked into the combustion-tube, and which retains the vapour of water from the hydrogen given up by the matter; and next, into an ordinary quintuple bulb arrangement, containing a solution of potash, which takes up the greater part of the carbonic acid that has been formed. The remaining carbonic acid (such, for instance, as may have been formed and delivered from the combustion-tube faster, owing to some occasional irregularity, than could be absorbed by the potash solution, and which we have found in appreciable quantity) is caught by, and increases the weight of the fragments of solid potash contained in the U-tube on the extreme left of the apparatus.

Finally, to complete the design which has been indicated in the calibration and graduation of the oxygen-reservoir, must be imagined a bent glass tube connected with the last-mentioned U-tube at one end, and leading into a mercury-trough under a suitable receiver, where all the remaining gases from the combustion-tube are at last gathered. As these gases can be only oxygen and nitrogen, they may be transferred from the receiver into a Volta or other eudiometer, where the volume of oxygen is determined either by detonating with hydrogen, by platinum sponge, or any other eudiometric mode that may be preferred. The volume of oxygen being thus known, the volume, and consequently the weight of the nitrogen that was in the receiver can be readily deduced.

In the meantime, the combustion being terminated, the platinum scroll, which now contains but the ashes of the matter, is withdrawn from the tube and weighed; the difference between the weight now found and the original weight of platinum alone is that of the ashes.

We have now the weight of earthy matter and of the four principal volatile matters which constitute the coal directly determined. And by the use of the graduated scale on the gasometer, we have also a check upon the general accuracy of the whole operation; for if the epochs have been carefully observed, the quantities of oxygen that by calculation must have been taken up in forming carbonic acid and water, should equal the whole quantity of oxygen directly observed to have been delivered from the gasometer during the process.

In illustration of what has been said as to the uniformity of results attainable by this method, we subjoin an extract from the note-book of weights obtained successively from two portions of the same sample of coal in two different experiments; the chloride of calcium tube having been changed in the interval, so as to afford a quite different initial weight, and thus having prevented any possibility of preoccupation in making the weighings.

Quantity of coal taken in each experiment, 0·5 gr.

	I.	II.
HO	0·25 gr.	0·24 gr.
CO^2 in bulbs	1·59	1·61
CO^2 in U-tube	0·06	0·04
Ash	0·02	0·02

Baltimore, Jan. 20, 1854.

Method of examining Butter. *By* Dr. L. von Babo.

The method of examining butter here described is only of use for the determination of its commercial value; it is calculated to enable a comparison of several samples of butter to be effected in a short time. The following instruments are required:—

1. For measuring the butter, a cylindrical glass tube, about $2\frac{1}{2}$ inches long and 2 lines wide, and open at both ends, is employed. It is ground in a conical form at one end and flat at the other. Into this is passed a cork attached to an iron wire, which closes the tube almost air-tight, but can be readily pushed through it. When in use, the cork is drawn back to the flat end of the tube, which is then filled by sticking it into a mass of butter; care must be taken to prevent the intrusion of air between the portions of butter. A mark is made on the tube to indicate the quantity of butter to be employed in the examination.

2. A graduated tube, $5\frac{1}{2}$ inches long, $2\frac{1}{2}$ lines wide, closed at one end and ground off at the other, is divided at the lower portion into ten equal parts, in such a manner that these ten parts may represent exactly the volume of butter contained in the other tube to the mark. In order to find this volume, the butter-measure is to be filled with water, whilst the stopper is placed exactly at the mark:

the water is then poured into the tube to be graduated; and after waiting for half a minute to make sure that all the water has collected, its level may be marked with a file, the height of the water being taken to its lowest point in the middle of the tube. The space below this mark is then divided into ten equal parts, and marked with a file. Another file-mark is made $3\frac{1}{2}$ inches above the graduation.

To test butter by means of this instrument, the measure is to be filled, as above described, by inserting it to a little above the mark. This is effected with thin pieces of butter, by inserting the tube perpendicularly into the butter on a plate until the edge of the tube comes in contact with the plate. The tube is then drawn back, and the stopper pushed down until the butter projects a little beyond the edge of the tube; and this operation is repeated until the tube gradually fills up. The mouth of the tube is then closed with the finger, and the cork pressed upon the butter until it is completely united; the cork is then pushed exactly to the mark, and the projecting portion of the butter scraped off. In this manner the presence of air is avoided. The butter-measure is then put over the open end of the graduated tube, and the butter pushed out of it by the stopper; any butter that may adhere to the latter is scraped off upon the edge of the graduated tube. The latter is then filled up to the mark with pure anhydrous æther, in which the butter is dissolved by shaking, the open end of the tube being closed by the finger. In about half a minute all the fat dissolves in the æther, whilst the impurities, such as buttermilk and water, are seen floating in the form of flakes or drops. If the tube be then left standing, all these impurities settle completely in about twenty-four hours to the bottom of the tube, forming a stratum the thickness of which may be ascertained by the divisions of the tube. Each division, as may be ascertained by experiments conducted in other ways, corresponds pretty exactly with 10 per cent. of impurities, whether these be water or other substances; and as half degrees may be easily marked, the quantity of butter may be determined to 5 per cent., or even still more exactly.

Middling samples of butter deposit a stratum of 2 degrees; they consequently contain 80 per cent. of butter and 20 per cent. of impurities; in bad samples, which however were still regarded as saleable, the stratum was not more than $2\frac{1}{2}$ degrees (75 per cent. of butter, 25 per cent. of impurities); some were examined in which the impurities rose to 3 and $3\frac{1}{2}$ degrees (70–75 per cent. of butter, 30–35 per cent. of impurities); and one sample even showed 4 degrees, and consequently only 60 per cent. of butter.

The author then gives a method by which the long standing of the samples is avoided. It consists in putting the tube with its contents into a tin box, and attaching it to a string, by means of which the whole is swung round in a circle, so as to hasten the separation of the two strata by the action of centrifugal force.—Dingler's *Polytechn. Journ.*, cxxx. p. 374.

THE CHEMICAL GAZETTE.

No. CCLXXIV.—March 15, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Contributions to the History of the Fatty Bodies. *By* J. Lefort.

In a former memoir, the author communicated his views on the composition of the fatty vegetable oils, and their behaviour with iodine, chlorine and bromine. He has since endeavoured to ascertain whether these elements do not act specially upon one of the constituents of the oils, as for example upon the oleine, rather than upon the margarine and stearine. He has arrived at the following results:—

Iodine, whose only action upon the fatty oils consists in depriving them of a very small portion of their hydrogen, does not appear to affect the oleine in any greater degree than the margarine and stearine. Chlorine and bromine, on the contrary, combine very readily with all the three principles.

These new compounds are heavier than water; chlorinated and brominated oleine are thicker than pure oleine, whilst the corresponding compounds of margarine and stearine do not possess so much consistency as the pure substances, and fuse at a much lower temperature. No reagent shows the presence of free bromine and chlorine in these compounds.

Stearine, margarine and oleine, under the influence of chlorine and bromine, lose the same quantity of hydrogen, which in the case of the first, the only one of which the exact composition is known, is 4 equivs. The author gives the formula $C^{76}\,H^{66}\,Cl^{4}\,O^{8}$ for chlorinated stearine, and for brominated stearine $C^{76}\,H^{66}\,Br^{4}\,O^{8}$. In the case of margarine and oleine, also, the chlorine and bromine would likewise displace 4 equivs. of hydrogen.

The author has also instituted some experiments on the action of the haloid elements upon the fatty acids.

Iodine has no action upon the fatty acids produced by the saponification of either the vegetable or animal oils. Chlorine and bromine also form no peculiar compounds with stearic and margaric acids if these be completely freed from oleic acid; small quantities of the elements are dissolved by the fatty acids, but no hydrochloric or hydrobromic acids are produced. Oleic acid, on the contrary, is readily acted upon, and furnishes the following compounds:—

Chlorinated Oleic Acid.—It is liquid at ordinary temperatures, heavier than water, and possesses a very strong brown colour; it

produces no precipitate with nitrate of silver. Its consistence is a little greater than that of the pure acid; its specific gravity, at a temperature of 46° F., is 1·082; it boils at 374° F. Its formula is $C^{36}\ H^{32}\ Cl^{2}\ O^{4}$.

Brominated Oleic Acid.—This possesses about the same consistence as the preceding; its colour is a darker brown, although reagents give no sign of the presence of free bromine when it has been well washed and not kept too long. Its specific gravity, at a temperature of 45°·5 F., is 1·272; it boils at 392° F. Its analysis gave numbers agreeing with the formula $C^{36}\ H^{32}\ Br^{2}\ O^{4}$.

The author considers that stearine and margarine belong to the class of isomeric compounds, and that the vegetable fatty oils are compounds in definite proportions of oleine and margarine, or perhaps rather oleomargarates of glycerine, the resolution of which may be effected by the most feeble agents.—*Comptes Rendus*, xxxvii. p. 28.

Researches on the Arsenæthyles. *By* H. Landolt.

[Concluded from page 89.]

The following contains a fuller description of the radicals and their compounds:—

I. *Arsenbiæthyle*, or *æthylokakodyle*, $As(C^{4}\ H^{5})^{2} = AsAe^{2}$, is a strongly refractive fluid, of a pale yellowish colour, which possesses an extremely disagreeable, penetrating, garlic-like odour. It sinks in water without mixing with it, but is readily soluble in alcohol and æther, and is completely precipitated from its alcoholic solution by an addition of water. Its boiling-point lies between 365° and 374° F.

As regards its power of combination, arsenbiæthyle resembles kakodyle, stibæthyle, &c.; when exposed to the air, it immediately attracts oxygen, and generally breaks out into a pale flame, with evolution of vapours of arsenious acid. Arsenbiæthyle, prepared according to the two methods above described, does not behave in exactly the same manner in this respect; for whilst a drop of the radical, prepared by distillation according to the first method, ignites immediately when allowed to fall upon wood or paper, that prepared by the second method, by precipitation from the alcoholic solution by water, only becomes ignited when heated to 356° F.

Arsenbiæthyle is especially distinguished from the other arsenæthyles by the circumstance, that by its imperfect combustion, as well as by its oxidation by dilute nitric acid, a red substance is always obtained as a secondary product, which corresponds with Bunsen's *erytrarsine*. This compound is of a pale red colour at the moment of its formation, but soon becomes darker; in the dry state it forms a brown powder, which becomes white by long exposure to the air. It is insoluble in water, alcohol and æther. When heated on platina foil, it burns with a pale arsenic-flame, and leaves no residue; when heated in a tube, it furnishes inflammable vapours of a disagreeable odour, and leaves a considerable residue of arsenic.

Another characteristic property of arsenbiæthyle is, that it imme-

diately reduces the oxides of the noble metals, which is not the case with arsentriæthyle. If an alcoholic solution of arsenbiæthyle be added to a solution of nitrate of silver, metallic silver is immediately separated; the oxides of mercury and other metals are similarly reduced.

The pure radical combines directly with the haloids, with considerable evolution of heat; and also with sulphur. Concentrated nitric acid oxidizes it, with production of fire. Concentrated sulphuric acid has no action in the cold, but when heated, sulphurous acid is evolved; dilute sulphuric acid has no action.

This radical resembles the corresponding kakodyle in its combining proportions, uniting like this with 1 atom of oxygen, chlorine, iodine, &c.; but the author cannot yet venture to speak with any certainty as to the existence of compounds with 3 atoms of those bodies.

All these compounds hitherto ascertained are fluid, and are particularly characterized by the possession of an extremely offensive permanent odour, strongly provocative of tears; this occurs with these in a much higher degree than with the compounds of any other arsenæthyle. Long exposure to this odour produces sneezing, continued running at the nose and headache.

Iodide of Arsenbiæthyle = $AsAe^2I$, is obtained by saturating an ætherial solution of the radical with a similar solution of iodine, and evaporating this fluid without access of air; it forms a yellow oil, which is readily soluble in alcohol and æther, but does not mix with water. When exposed to the air, this compound does not fume; when heated, it ignites with some difficulty, with evolution of vapours of iodine. Its alcoholic solution immediately furnishes a precipitate of iodide of silver with nitrate of silver; when mixed with a solution of bichloride of mercury in watery alcohol, no precipitate is produced.

The tendency to form double compounds appears to belong to arsenbiæthyle in an equally high degree with kakodyle.

II. *Arsentriæthyle*, $As(C^4H^5)^3 = AsAe^3$.—This radical is obtained in much greater quantity than arsenbiæthyle. Its preparation is best performed by the first method, in which the arseniuret of sodium is treated with iodide of æthyle, and distilled dry; the mixture of arsentriæthyle and arsenbiæthyle obtained is submitted to a fractional distillation, when the former passes over between 284° and 354° F.

In this manner the pure radical is obtained as a colourless, strongly refractive, very mobile fluid, possessing a disagreeable odour like that of arseniuretted hydrogen gas, mixing readily with alcohol and æther, but insoluble in water. Arsentriæthyle begins to boil at 284° F. under a pressure of 736 millimetres, but the boiling-point gradually and slowly rises to 354° F., whilst some metallic arsenic is deposited. Decomposition consequently takes place during the distillation; this however is on the whole very inconsiderable, for different portions collected at 284° and 336° F. exhibited at the utmost a difference of 1 per cent. in the quantity of carbon.

At a temperature of 62° F. the specific gravity of the fluid arsentriæthyle is 1·151. The specific gravity of the vapours of arsentri-

æthyle was ascertained by Gay-Lussac's method, which was also employed by Bunsen for many kakodyle compounds; Dumas' process is not applicable to this case, partly from the great oxidizability of the compound, and partly also from the large quantity of the substance required. The graduated tube, filled with boiled mercury, in which the glass bulb containing the substance had been previously allowed to ascend, was surrounded by a column of oil, and this was brought to the required temperature in the usual manner by heating the iron mercurial trough. The experiment gave the following result:—

Quantity of substance employed	0·1745 grm.
Measured volume of vapour	51·0 cub. centims.
Temperature of the vapour	349°·7 F.
Height of the mercury in the graduated tube above the level of the trough at 349°·7 F.	118 millims.
Height of the column of oil	221 ...
Height of the barometer at 54°·6 F.....	726·7 ...

From this the specific gravity of the vapour of arsentriæthyle, after taking into consideration all corrections, appears to be 5·2783, which agrees pretty well with the result of calculation, 5·6276. Thus—

	Vols.	Spec. grav.
3 atoms. of æthyle gas	6	12·1110
1 atom of arsenical gas.....	1	10·3995
1 atom of arsentriæthyle gas	4	22·5105

22·5105 : 4=5·6276.

Arsentriæthyle approaches very closely to arsenbiæthyle in regard to its power of combination. If the pure radical be exposed to the contact of the air, it fumes and becomes heated at first, but rarely breaks out into flame; spontaneous ignition usually occurs only when it is gently heated. The products of its combustion are arsenious acid, carbonic acid and water. From this ready oxidizability, it is difficult to obtain arsentriæthyle in a pure state; when it has been kept for some time, even under water, in a well-stopped vessel, there is usually more or less oxide mixed with it; this may be known by fumes being no longer produced on exposure to the air.

If concentrated nitric acid be poured upon the radical, oxidation takes place with strong explosion and flame. When mixed with nitric acid of spec. grav. 1·42, it dissolves gradually with a slight evolution of nitric oxide gas, and nitrate of oxide of arsentriæthyle is obtained; a product analogous to erytrarsine is not formed in this case, any more than during oxidation in the air. Arsentriæthyle mixes with concentrated sulphuric acid, and reduces it to sulphurous acid when heated. The oxides of the noble metals are not reduced by the radical; its alcoholic solution consequently produces no separation of metallic silver when added to solution of nitrate of silver.

Compounds of Arsentriæthyle.—Arsentriæthyle agrees exactly

in its combining proportions with the corresponding stibæthyle; like this, it unites with 2 atoms of chlorine, bromine, iodine and sulphur, and with 2 atoms of oxygen furnishes a base which saturates 2 atoms of acid. Of these compounds, for the preparation of which the pure radical should be employed, the author has as yet examined the following:—

Oxide of Arsentriæthyle, $As(C^4 H^5)^3 O^2 = AsAe^3 O^2$.—If an ætherial solution of the radical be allowed to evaporate slowly in the air at the ordinary temperature, the oxide remains in the form of a nearly colourless oily fluid, of a slight garlic-like odour. This is however not pure, but contaminated with other products of oxidation, which have not yet been examined. Larger quantities of oxide of arsentriæthyle are very easily prepared by extracting the mass obtained by the action of iodide of æthyle upon arseniuret of sodium, first with æther and afterwards with alcohol, evaporating the alcoholic extract, and submitting the residue to dry distillation in a retort. It then appears also in the form of a slightly yellowish oily fluid, which sinks in water, and does not mix with it; it is however readily soluble in alcohol and æther. It is separated unchanged from its alcoholic solution by the addition of water.

When the compound is exposed to the air, it becomes turbid and more highly oxidized, but without giving off fumes or igniting. Its alcoholic solution has no reaction upon litmus-paper, and gives no precipitate with solution of nitrate of silver. It is readily dissolved by tolerably dilute nitric acid, but is insoluble in dilute sulphuric and muriatic acids.

When pure arsentriæthyle is allowed to stand for several weeks in a loosely-stopped bottle, beautiful tabular crystals are gradually formed on the surface; and if, as soon as a crust of these crystals has formed, it is made to sink to the bottom of the fluid, nearly the whole of it may at last be converted into this solid compound. The crystals are completely inodorous, and soluble in æther and alcohol; but when brought into contact with water, they deliquesce again into a colourless oil, which remains undissolved; this liquefaction also takes place in moist air, and on the application of a gentle heat. This compound has an acid reaction; with a solution of nitrate of silver, its alcoholic solution gives a yellow flocculent precipitate, which diminishes greatly in drying, and then forms a brown powder. It contains 60·8 per cent. of silver. Two elementary analyses, for which there was sufficient material, gave discordant results, so that nothing further can be stated as to the composition of this substance.

Sulphuret of Arsentriæthyle, $As(C^4 H^5)^3 S^2 = AsAe^3 S^2$.—If an ætherial solution of arsentriæthyle be boiled in a retort with washed flowers of sulphur, and the fluid, after the excess of sulphur has settled to the bottom, be poured into another vessel and left to cool there, beautiful columnar crystals of the sulphur compound are deposited. If much æther has been employed, the crystals are only separated on evaporation. They are usually contaminated with sulphur, and also with a little adherent oxide of arsentriæthyle, which latter is very difficult to get rid of. The best plan is to recrystallize

the compound from alcohol or water, when the compound separates in small plumose crystals; if it be desired to obtain larger crystals, the small ones are dissolved again in hot æther, and the solution is allowed to evaporate slowly.

Sulphuret of arsentriæthyle is readily soluble in alcohol, and also in hot water and boiling æther, but is nearly insoluble in cold æther. Its taste is bitter; in the pure state it is quite inodorous.

When exposed to the air, this compound does not undergo the least change. Concentrated nitric acid acts upon it very violently; the sulphur becomes oxidized into sulphuric acid, but the arsentriæthyle is not completely oxidized. Dilute muriatic acid evolves some sulphuretted hydrogen, with formation of a small quantity of chloride of arsentriæthyle, which is recognized by a penetrating odour; the decomposition however is not complete. The watery solution of sulphuret of arsentriæthyle immediately produces a black precipitate of sulphuret of silver with a solution of nitrate of silver; but no precipitate is produced in solutions of acetate of lead or of copper salts. In protonitrate of mercury a black precipitate is produced, which gradually becomes white; in solution of bichloride of mercury a voluminous white precipitate is formed. Sulphuret of arsentriæthyle is a very permanent compound; when boiled with solution of potash, no decomposition is produced; it merely melts, and solidifies again on cooling into a crystalline mass. A watery solution of pentasulphuret of potassium even abandons sulphur when boiled with oxide of arsentriæthyle; the fluid becomes colourless, and on cooling, crystals of sulphuret of arsentriæthyle separate.

If the compound be heated in a tube, it fuses at a little above 212° F. into a yellowish fluid, which when further heated begins to boil, and gives off a quantity of fumes, which ignite on coming in contact with the air; during this process a yellowish-red coating of sulphuret of arsenic is formed in the tube. Analysis gave:—

Arsenic	..	..	1 =	75	38·66
Carbon	..	..	12	72	37·11
Hydrogen	..	..	15	15	7·73
Sulphur	16·17	15·77	2	32	16·50

Iodide of Arsentriæthyle, $As(C^4 H^5)^3 I^2 = AsAe^3 I^2$.—When an ætherial solution of iodine is added to an ætherial solution of arsentriæthyle as long as decolorization is produced, this compound separates in large quantities in the form of a flocculent precipitate of a sulphur-yellow colour. This is immediately separated from the fluid, washed with æther, pressed between blotting-paper, dried by a very gentle heat, and then kept in a well-stoppered bottle.

This compound is very unstable; if exposed to the air only for a short time, it becomes brown, and soon deliquesces into a dark-coloured fluid of the consistence of a syrup; even when the air is completely excluded, it gradually becomes brown. It is readily soluble in water and alcohol, but dissolves in æther with great difficulty. Nitric and sulphuric acids decompose it immediately, with separation of iodine; it is soluble in muriatic acid with the assistance

of heat, but separates again unchanged on cooling; the iodine is abstracted by concentrated solution of potash, oxide of arsentriæthyle being formed.

When this compound is heated in a tube, it acquires a dark colour, and fuses at 320° F. into a brown fluid, which again becomes solid on cooling; when heated to 374° F., it becomes converted, with partial decomposition, into vapours, which condense in the cooler portions of the tube into pale yellow drops; no separation of iodine was observable during this process.

The watery solution of iodide of arsentriæthyle immediately produces a precipitate of iodide of silver with nitrate of silver; iodide of lead is also separated by it from solution of acetate of lead. In solution of bichloride of mercury a white precipitate is produced, which is soluble in an excess of the solution. Analysis:—

Arsenic..	..	..	..	1 =	75	18·03
Carbon ..	17·68	..	..	12	72	17·31
Hydrogen	4·14	..	..	15	15	3·60
Iodine ..	60·98	60·74	60·19	2	254	61·06

Chloride of Arsentriæthyle.—Only traces of this compound could be obtained; a process for its preparation in larger quantities is still a desideratum. If an alcoholic solution of oxide of arsentriæthyle be mixed with concentrated muriatic acid, and water be afterwards added to the mixture, the oxide is separated again unchanged; yet the fluid acquires an insupportable odour, which strongly affects the eyes, and which does not belong to arsentriæthyle; it can consequently only arise from a small quantity of the chloride. The compound could not be obtained by the decomposition of the iodide of arsentriæthyle by bichloride of mercury.

Nitrate of Oxide of Arsentriæthyle is obtained by treating the pure radical or its oxide with dilute nitric acid. When the fluid is evaporated on the water-bath, a thick syrup is obtained, from which crystals are deposited after long standing under the exsiccator; they quickly attract water, and deliquesce when exposed to the air.

III. *Arsenæthylium.*—The mode of formation of this radical is analogous to that of stibæthylium and stibmethylium; 1 atom of arsentriæthyle combining with 1 atom of iodide of æthyle to form iodide of arsenæthylium ($AsAe^4I$). Pure arsenæthylium is not known; in its compounds it presents a complete conformity with stibmethylium, and consequently also with potassium and ammonium. Arsenæthylium combines with 1 atom of chlorine, bromine and iodine, to form crystallizable salts; with 1 atom of oxygen it furnishes a base, which approaches very closely to potash in respect to its alkaline properties, and forms neutral and acid salts with acids. These compounds are characterized by the ease with which they crystallize, and by their great stability; they do not change in the least when exposed to the air; they are all perfectly inodorous, and dissolve very readily in water. Their taste is bitter, and they do not appear to possess any poisonous properties. All these peculiarities serve to distinguish them from the compounds of arsenbiæthyle and arsentriæthyle.

The author has hitherto analysed the following salts of arsenæthylium:—

Iodide of Arsenæthylium, $As(C^4 H^5)^4 I = AsAe^4 I$.—When arsentriæthyle and iodide of æthyle are mixed together, this compound is generally produced in a few hours; it is formed more rapidly in the cold, and the entire fluid solidifies in crystals. Iodide of arsenæthylium, which is readily obtained in considerable quantity by the two methods already given for the preparation of the arsenæthyles, usually crystallizes in long colourless needles, which after long keeping often acquire a dark colour. They are readily soluble in water and alcohol, but insoluble in æther and in alcohol containing æther. The salt behaves exactly like iodide of potassium; iodine is immediately separated by nitric acid, and also by sulphuric acid, which also sets free hydriodic acid and sulphurous acid. When the crystals are heated, they fall to powder, and white fumes, which ignite when in contact with the air, are evolved, whilst metallic arsenic is sublimed; only a very slight separation of iodine or iodide of arsenic is observable.

If a watery solution of iodide of arsenæthylium be brought into contact with an excess of freshly-prepared hydrated oxide of silver, iodide of silver is immediately formed, and the solution contains *oxide of arsenæthylium*. If the fluid be filtered and evaporated with as little access of air as possible, the compound remains in the form of a white mass, which has a very strong alkaline reaction, and rapidly attracts water and carbonic acid when exposed to the air. The alkaline properties of the oxide of arsenæthylium are just as strong as those of oxide of stibmethylium; even in the cold it separates ammonia from its salts; and the earths, as well as the oxides of the heavy metals, are also precipitated by it from their solutions.

Chloride of Arsenæthylium, $AsAe^4 Cl + 8HO$.—This compound cannot be obtained by the decomposition of iodide of arsenæthylium by chloride of mercury, as when the two solutions are brought together, no iodide of mercury, but a white double compound is thrown down. The salt is best prepared by the saturation of a solution of oxide of arsenæthylium with dilute muriatic acid; on the evaporation of the fluid, crystals are produced, which contain water of crystallization, and deliquesce very rapidly when exposed to the air. They have a bitter taste, and are very readily soluble in alcohol and water, but insoluble in æther. Concentrated sulphuric acid immediately evolves muriatic acid gas from this compound. Nitrate of silver immediately produces a precipitate of chloride of silver in the watery solution of the salt; solution of bichloride of mercury throws down a white insoluble double compound. If the crystals be heated, they first melt in their water of crystallization, then lose this by degrees, whilst a decomposition commences; the salt is at length entirely dissipated from the formation of volatile products.

The water of crystallization of this salt cannot be directly determined, as when it is expelled by heat the decomposition of the chloride of arsenæthylium takes place simultaneously with its expulsion. If a watery solution of the salt be evaporated under the

air-pump with sulphuric acid, there remain crystals, which according to the amount of chlorine appear to contain 8 atoms of water of crystallization:—

Arsenic	..	..	1 =	75·0	25·13
Carbon	..	..	16	96·0	32·16
Hydrogen	..	..	20	20·0	6·70
Chlorine	11·88	11·98	1	35·5	11·89
Water	..	..	8	72·0	24·12

Bisulphate of Oxide of Arsenæthylium, $AsAe^4O, HO, 2SO^3$, was obtained by the precipitation of iodide of arsenæthylium with a solution of sulphate of silver, containing an excess of sulphuric acid. After filtration and evaporation, granular crystals remain, which may be obtained pure by repeated recrystallizations. This salt is readily soluble in water and alcohol, but is difficult of solution in æther; its taste is at first sour, but afterwards bitter. When heated in a tube, it first of all fuses with a crackling, and then furnishes acid fumes, which do not ignite in the air:—

Arsenic	..	..	1 =	75	26·04
Carbon	33·05	..	16	96	33·33
Hydrogen	7·55	..	20	20	6·94
Oxygen	..	..	1	8	2·78
Water	..	..	1	9	3·13
Sulphuric acid	28·23	28·27	2	80	27·78

Dissertation, Breslau, 1853.

On Æthylamine. *By* Prof. Wöhler.

Æthylamine is more readily obtained than by many of the known methods, by mixing iodide (and perhaps also bromide) of æthyle with an equal quantity of absolute alcohol, and passing into the mixture a stream of dry ammoniacal gas, whilst heated to boiling in a proper apparatus for the prevention of evaporation. On cooling, it is completely saturated with ammoniacal gas, and left standing for a few days, until the addition of water no longer produces a turbidity in the fluid. It is evaporated to dryness on the water-bath, decomposed by potash, and the gaseous æthylamine conducted into water; or if it be desired to have it pure, it is passed, after being dried, into a U-tube artificially cooled.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 374.

Chemical Notices. *By* Alexander Kemp, F.R.S.E., *Assistant Teacher of Chemistry in the University of Edinburgh**.

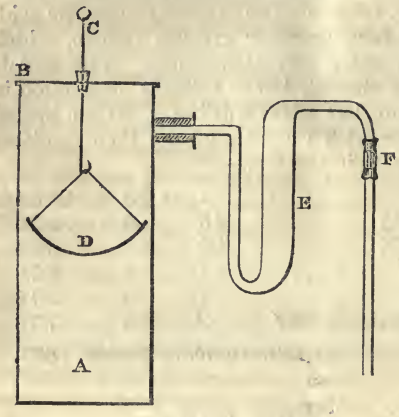
Sulphuretted Hydrogen Apparatus.

The object of the instrument now about to be described is to furnish a supply of clean-washed sulphuretted hydrogen gas, for any

* Communicated by the Author.

length of time for which it may be required, as well as to avoid the escape of any gas after the operation in which it has been used is completed. Every chemist knows that this gas is one of our most valuable reagents, and probably, next to water or hydrochloric acid, is the one most frequently used in inorganic analysis; and that a solution of it in water is employed on many occasions, in order to avoid the trouble of charging an apparatus for preparing the gas at the time.

The construction of the instrument will be most easily understood from the accompanying sketch:—



A is a glass jar, with a lateral tubulure near the top. B is a circle of plate glass, fitting air-tight upon A, the upper edge of which is ground to receive it; in the centre of this plate a hole is drilled to hold a cork, through which the wire C is passed so as to admit of its sliding freely; and from this wire a perforated cup of lead or earthenware, D, is suspended. E is the washing tube, and F a caoutchouc connector for attaching a clean tube when requisite.

In using this apparatus, a quantity of dilute sulphuric or hydrochloric acid is poured into A until it fills it about one-third from the top; some sulphuret of iron is next placed in D, and the glass plate is then placed on the top of the jar, taking care that D does not come in contact with the acid. When gas is required, the washing tube E, containing a little water, is fitted to the tubulure, and D is then slowly depressed, by means of the wire C, until it just touches the liquid. If only a few bubbles of gas are to be made use of, it must be immediately drawn up again, as sufficient acid will have entered by the holes in D, and adhered to the sulphuret to produce them. When large and continuous quantities are wanted, then D may be fully immersed, but not far below the surface, because the salt of iron formed being denser than the acid liquid will fall down through the perforations in D, and so allow fresh acid to take its place to continue the action.

After the apparatus has been laid aside, it is at any time fit for use, as the gas contained in the upper part is confined by the water in the washing-tube, which acts as a kind of valve. In order that the glass plate B may be firmly kept in its place, a weight may be placed on it, or better, an india-rubber band may be put under the tubulure, stretched across B, and fastened to the opposite side of the jar by a wire or cord passed round it just underneath the rim.

Oxide of Copper.

The ordinary method of preparing this substance as it is used in organic analysis is to heat the nitrate of the metal to ignition in a crucible; this is attended with much inconvenience, owing to the salt melting, frothing, and in general flowing over the sides of the vessel; in addition to which the crucible commonly cracks during the operation, and permits the liquid portion to run through into the fire. Now all this may be avoided by using a vessel of copper, which is easily made by any one, by simply taking a piece of sheet copper, and folding it so as to form a water-tight vessel without the use of solder; every one, I believe, knows how this is to be done; if not, inspecting a common kitchen fire-shovel will render this intelligible.

In a vessel of this description the nitrate may be safely decomposed, and without any risk of overheating and fusing the oxide; and although the vessel gradually wears out in so doing, it yields a quantity of oxide of copper, which is mixed along with that produced from the nitrate. I may add, that this method has now been followed for five or six years in the laboratory of the Edinburgh University ; and as I have never met with any one who knew it, I thought it worth description.

On Permanganic Acid. By Prof. Wöhler.

When perfectly-concentrated sulphuric acid is poured over a considerable quantity of crystallized permanganate of potash, the latter is decomposed with the evolution of much heat, red flames burst forth, and peroxide of manganese is formed, which, like oxide of zinc, flies off into the air. Pure oxygen gas is evolved during the action. Permanganic acid must therefore exist in a gaseous state. The author also refers to a similar observation already made by Unverdorben.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 373.

Determination of the per-centage of Tannin in Substances used for Tanning. By Prof. Fehling.

Among the various substances which precipitate tannin from solution, such as gelatine, quinine, animal skin, &c., the latter has hitherto been recommended as the most appropriate for determining the per-centage of tannin. This method of valuation has been preferred, because it represents in miniature the operation to which the results refer. There are, however, no detailed directions for its application; and in repeated trials made by the author, under a variety of conditions, he has found that the tannin is never perfectly precipitated, and that the solutions soon become mouldy. Experiments with solution of quinine, freshly-precipitated oxide of iron or alumina, did not give more satisfactory results. He then tried gelatine in solution; and instead of weighing the precipitate obtained, by adding an excess of gelatine, preferred adopting the volumetrical

method, estimating the quantity of solution of gelatine of known centigrade value required to precipitate the tannin. For this purpose it is indispensable that the precipitate should separate readily; but with most kinds of tannin this is not the case. The author has found it advantageous to use a dilute solution of gelatine, and to have the liquids quite cold. His mode of operating is as follows:—

The solution of gelatine is prepared by digesting 10 grms. of dry gelatine (containing about 18 or 19 per cent. of water) in water for twelve hours, and then applying heat until the solution is complete. The volume is then made up to 1 litre.

For the purpose of determining the centigrade value of the gelatine solution, 0·2 grm. of pure tannic acid, dried at 212° F., is dissolved in 100 or 120 grms. of water, and the gelatine solution added from a graduated burette until the precipitation is complete. Filtration is generally necessary towards the end of the operation, or as a substitute, the following plan may be adopted:—A narrow open glass tube is covered at one end with some tolerably thick linen bound tight by cord; on immersing this covered end in the liquid, and sucking out the air by the mouth at the other end, a portion is rendered clear by passing through the linen, and may be poured into a tube, and tested with gelatine.

The author found that the 0·2 grm. of pure dry tannic acid required from 32·5 to 33 cub. centims. of the gelatine solution for perfect precipitation; when the gelatine solution is some days old, a larger quantity is necessary, 35, 38, or even 40 cub. centims. It is therefore necessary in all cases, when the gelatine solution has been kept any time, to determine its centigrade value by means of tannic acid immediately before making any experiments with it.

If it is required to estimate the value of oak or other barks for tanning, they are first dried in a warm room, powdered finely, digested in quantities of 10 grms. with warm water, and exhausted by means of a displacement apparatus, constructed of a tube 2 feet long, 1 inch wide, and drawn out at the lower end, which is loosely stopped with cotton wool. Some substances may be introduced dry into this apparatus, and exhausted by warm or cold water. The extraction may likewise be facilitated by the pressure of a column of water, applied by fitting a narrow glass tube with a cork into the upper end.

In most cases the extraction is completed in one or two days. When the operation is properly conducted, the quantity of liquid extract amounts to half a pound or a pound. It is then treated with gelatine solution so long as a precipitate is produced. A few drops of dilute hydrochloric acid facilitate the separation of the coagulum.

The quantity to be taken for an experiment of substances rich in tannin, such as galls, is about 0·5 or 1·0 grm. A simple calculation gives the per-centage of tannin.

The author states that he has adopted this method in repeated examinations of tanning materials during the last ten years; he has found the results tolerably constant, and, notwithstanding its apparent imperfection, more trustworthy than any other yet known.

He estimates the relative value of several substances of this kind as follows:—

Pine bark contains from.....	5 to 7	per cent.	tannin.
Old oak bark contains	9	...	...
Best oak bark contains from ..	19 to 21	...	...
Gall nuts contain from	30 to 33	...	...
Aleppo galls contain from	60 to 66	...	...
Chinese galls contain.....	70	...	...

These data at least admit of comparison with each other, and indicate with tolerable certainty the respective value of these substances to the tanner. This method of valuation is indeed based upon the assumption that the same kind of tannin exists in all these substances. It is, however, extremely probable that this is not the case; but, at the same time, it may fairly be assumed, that if different kinds of tannin combine under similar conditions with different quantities of gelatine, they will also combine with animal skins in the same relative proportions. If, therefore, this method does not indicate the absolute per-centage of tannin, it still gives the per-centage value of the substance examined; and it is precisely this which the tanner requires.

It is another question, whether gelatine solution precipitates all the substances of the tanning material which combine with the skin; and it therefore remains to be determined by experience whether such a method of valuation is sufficient for the purposes of the tanner.—*Polytechnisches Central Blatt*, 1853; and *Pharmaceutical Journal.*

On some Constituents of Frog's Flesh. By F Grohé.

According to the author's investigations, neither urea nor oxalic acid exist in the flesh of the frog. The crystals supposed by Moleschott to consist of those substances are creatine, creatinine, and nitrate of potash. In other respects it contains the same constituents as other kinds of flesh.—*Ann. der Chem. und Pharm.*, lxxxv. p. 233.

Contributions to the knowledge of some Volatile Bases.
By Dr. A. von Planta *and* Dr. Aug. Kekulé.

The authors have treated nicotine with iodide of æthyle. The two substances act upon each other even at ordinary temperatures; and when the mixture is exposed to the heat of boiling water, which is best done in closed tubes, the reaction is completed in an hour. It is best to employ an excess of iodide of æthyle. In this way crystals of iodide of æthylonicotine are obtained, together with a product of decomposition of a red colour, also containing iodine.

Iodide of Æthylonicotine, $C^{14}H^{12}NI$, forms deliquescent crystals, which are but sparingly soluble in alcohol and water. It is obtained, on the cooling of its hot alcoholic solution, in beautiful colourless columns, grouped in warts; and also when the iodide of

æthyle and nicotine are diluted with alcohol when acting upon each other:—

Carbon	..	..	14 =	84·0	35·43
Hydrogen	..	..	12	12·0	5·06
Nitrogen	..	..	1	14·0	5·90
Iodine	53·81	53·28	1	127·1	53·61

Bromide of Æthylonicotine also forms crystals, which are still more deliquescent than the iodide, and tolerably soluble in absolute alcohol.

Æthylonicotine.—Neither the bromide nor the iodide are decomposed by potash; but by treating either of these compounds with freshly-precipitated oxide of silver, æthylonicotine is obtained. It has a strongly alkaline reaction; when concentrated, it acts upon the epidermis like solution of potash; it has an extremely bitter taste, and possesses no smell. With saline solutions it acts like a fixed alkali; it expels ammonia from its compounds, and precipitates the metallic oxides and alkaline earths. Its watery solution acquires a colour even by standing in the air; it cannot be concentrated by evaporation, as it acquires a deep reddish-brown colour, and deposits thick brown drops, which are soluble in water with difficulty, and possess an odour of putrid fish. The salts of this base are soluble in water; tannic acid produces no precipitate; picric acid, a sulphur-yellow flocculent one. The muriate crystallizes; but the other salts formed with sulphuric, nitric, and oxalic acids crystallize with difficulty, or form a thick syrup. The acetate is completely uncrystallizable.

Perchloride of Æthylonicotine and Platinum, $C^{14}H^{12}NCl + PtCl^2$ or $C^{10}H^7(C^4H^5)NCl + PtCl^2$, is precipitated in yellow flakes, and also forms rhombic columnar crystals, of an orange-red colour. This compound is insoluble in alcohol and æther. Analysis:—

C	26·61	..	..	27·36	27·35	14 = 84·0	26·65
H	3·94	..	..	4·08	4·15	12 12·0	3·81
N	..	..	..	..	..	1 14·0	4·44
Cl	..	..	..	..	..	3 106·5	33·79
Pt	..	31·26	31·33	31·27	31·53	1 98·7	31·31

Perchloride of Æthylonicotine and Gold.—Chloride of gold, added to the muriate of the base, furnishes a precipitate of a sulphur-yellow colour, which is obtained on the cooling of its solution in hot water, in beautiful, golden-yellow, acicular crystals. On analysis it furnished:—

Carbon	..	..	14 =	84	18·71
Hydrogen	..	..	12	12	2·67
Nitrogen	..	..	1	14	3·12
Chlorine	..	..	4	142	31·63
Gold	43·87	43·99	1	197	43·87

Chloride of Æthylonicotine and Palladium.—Chloride of palladium does not produce a precipitate with the muriate of the base; on evaporation, a brown gum-like mass is obtained, which, when dissolved in alcohol, furnishes large brown rhombic prisms by spontaneous evaporation.

Perchloride of Æthylonicotine and Mercury.—Solution of bichloride of mercury produces a white flocculent precipitate in the solution of the muriate of the base; this soon collects into a resinous mass, and fuses when heated. It is soluble in boiling water, from which it crystallizes; the crystals may be washed with cold water. Analysis:—

Carbon	15·39	14 =	84	15·22
Hydrogen	2·25	12	12	2·17
Nitrogen	..	1	14	2·54
Chlorine	25·71	4	142	25·72
Mercury	54·14	3	300	54·35

According as the formula $C^{10}H^7N$ or $C^{20}H^{14}N$ is attributed to nicotine, the other bodies are either—

Æthylonicotine $= C^{14}H^{11}N = C^{10}H^6(C^4H^5)N$,
or perhaps more correctly $= C^{14}H^{12}NO$,

or, Æthylonicotine $= C^{28}H^{22}N^2 = C^{20}H^{12}(C^4H^5)^2N^2$,
$= C^{20}H^{13}(C^4H^5)^2N^2O$.

When heated iodide of æthylonicotine becomes decomposed into iodide of æthyle and nicotine. During this operation, the two products of decomposition may again combine to reproduce the iodide of æthylonicotine.

As regards the constitution of æthylonicotine, the authors conclude,—1st, from the circumstance that potash does not separate any oleaginous body from the solution of the iodide and bromide; 2nd, from the above-mentioned decomposition of the iodide by heat; and 3rd, from the want of odour in the base and the crystallizability of the salts—that æthylonicotine belongs to the fourth of Hofmann's series, and that it is consequently related to nicotine in the same way that tetræthylammonium is to triæthylamine. If nicotine itself be regarded as $C^{10}H^7N$, it must belong to the third of Hofmann's series; that is to say, it must be a nitryle base, in which the carbon and hydrogen ($C^{10}H^7$) act the part of the 3 equivs. H in ammonia. In fact, a repeated treatment of æthylonicotine with iodide of æthyle supports such a composition, for it took up no more æthyle.

The compound formed by the heating of the watery solution of æthylonicotine is a reddish-brown oil; on distillation, it furnishes a brown oil, and a watery fluid of a strong alkaline reaction, which is of a deep red colour by transmitted, and green and iridescent by reflected light; both colour the skin yellow, and have an extremely penetrating odour like putrid fish.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 1.

On Protiodide of Tin. By Prof. Wöhler.

Prof. Wöhler states, from experiments made by Dünhaupt, that protiodide of tin is obtained in fine shining prisms, when strips of tin foil are kept boiling with rather concentrated hydriodic acid in a long glass tube closed at one end, or heated to 248°–302° F. in a closed tube.

When iodide of amyle was treated in the same manner at 356° F. in a closed tube, the tin foil in that portion of the tube which was most rapidly cooled bore shining, yellowish-red, quadratic octohedra, whilst that in the other portion of the tube which stood in the oil was covered with sulphur-yellow prisms. Both bodies were perhaps dimorphous forms of protiodide of tin. At the same time a very peculiar substance, of a powerful odour, perhaps stannamyle, was formed. The substances produced are as yet uninvestigated.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 374.

ANALYTICAL CHEMISTRY.

Detection of Poppy- or Nut-Oil in Olive-oil. By E. Marchand.

In consequence of the frequent adulteration of olive-oil, the author had occasion to examine the various methods of detecting it, and has found that the use of sulphuric acid gave satisfactory results.

He describes the process thus:—When 4 drops of olive-, poppy-, or nut-oil are placed separately upon a slab of porcelain, and 2 drops of pure concentrated sulphuric acid added, and mixed with the oils by inclining the slab to one side and the other, the following phænomena are observed:—

Olive-oil acquires, at the points of contact with the acid, a yellow colour passing into orange; the liquid portion surrounding the magma rapidly becomes dirty gray, and then brownish-black, while the yellow colour first produced by the acid gradually passes into bright chestnut-brown. There is never any appearance of blue or lilac tints.

Poppy-oil acquires, immediately at the points of contact with the acid, a fine lemon-yellow colour, which becomes rapidly darker at some parts. The liquid portion in contact with the coloured portions never acquires the dirty gray colour characteristic of olive-oil. After the reaction has continued for ten or fifteen minutes, there is observed, at several points of the liquid portion which immediately borders upon the coloured part, a rose colour, passing rapidly into bright lilac, and gradually increasing in intensity. After half or three-quarters of an hour, the lilac colour passes into a violet-blue, while the original yellow gradually becomes dull brown.

Nut-oil behaves almost exactly the same as olive-oil, except that the yellow substance is more abundant, more rapidly formed, and becomes brown more rapidly, so that within less than ten minutes it acquires a chestnut colour. Sulphuric acid is far more easily miscible with this oil than with olive- or poppy-oil. The gray border, which is characteristic of olive-oil, is produced with nut-oil as well; but in this case, instead of gradually becoming black, it passes rapidly into olive-green. This oil never produces a tint of lilac.

Mixtures of Olive- and Poppy-oils may be tested by means of the

above reactions. After a certain time, the colours characteristic of poppy-oil, pink, lilac, violet, blue, present themselves successively, with an intensity proportionate to the quantity of poppy-oil present. Marchand states, that with practice, one-tenth poppy-oil in olive-oil may be detected with certainty by this method.

Mixtures of Olive- and Nut-oils.—When the nut-oil amounts to one-fourth of the whole, sulphuric acid produces a bright orange-yellow colour, with a gray border, the outermost parts of which pass into olive-green. A mixture of equal parts of both oils gives an orange-yellow colour, with a very distinct gray border, which soon becomes greenish and brown at the outer edge. When the mixture contains three-fourths nut-oil, a reddish-yellow colour is produced, surrounded by an olive-green border, paler than that produced with pure nut-oil.

Mixtures of Poppy- and Nut-oils acquire with sulphuric acid a yellow colour, and at the borders a grayish tint, gradually diffusing itself over the liquid part. When the mixture contains one-fourth nut-oil, an intense lilac is subsequently produced, while the yellow colour passes into chestnut-brown. When the mixture contains three-fourths nut-oil, an orange-yellow is produced, with gray borders, passing at certain points into olive-green. Subsequently the yellow becomes bright chestnut-brown.—*Journ. de Pharm.*, October 1853; and *Pharmaceutical Journal.*

PROCEEDINGS OF SOCIETIES.

Royal Society.

Jan. 12, 1854. (The Lord Chief Baron, V.P., in the Chair.)

A paper was read, entitled "On some New and Simple Methods of detecting Manganese in Natural and Artificial Compounds, and of obtaining its Combinations for œconomical or other uses." By Edmund Davy, Esq., F.R.S., M.R.I.A. &c.

In this paper the growing importance of manganese since its discovery, and its extensive distribution in nature are noticed. Manganese is chiefly found combined with oxygen, but its oxides are commonly mixed with those of iron, and though different methods of separating them have been recommended, yet no very simple or unobjectionable test for manganese seems to be known. Two methods for detecting manganese are recommended, viz.—

1. The pure hydrated fixed alkalies, potash and soda, and especially potash. 2. Sulphur.

With regard to the first method. Though the compound *Chameleon mineral* made by strongly heating nitre or potash and peroxide of manganese together, has long been known, yet it appears hitherto to have escaped observation, that potash seems to be a more delicate test of manganese than any other known substance. The use of potash in this way is simple and easy; it is employed in solution; equal weights of the alkali and water

form a fluid well-adapted for the purpose; different metals may be used in the form of slips on which to make the experiments, but a preference is given to silver foil, as it is less acted on by alkalies than platina, and is more readily cleaned. A slip of such foil, about two or three inches in length and half an inch wide, answers well. Solids, to be examined for manganese, are finely pulverized; fluids require no preparation; the smallest portion of either is mixed with a drop or part of a drop of the alkali on the foil and heated by a spirit-lamp (for many experiments a candle affords sufficient heat), when on boiling the alkali to dryness and raising the heat, the characteristic green manganate of potash will appear on the foil. The delicacy of the alkali as a test thus applied, will be obvious on using the most minute portions of manganese ores in fine powder, and the author's son, Dr. E. W. Davy, readily detected manganese in a single drop of a solution containing one grain of solid sulphate in ten thousand grains of water. The presence of other oxides do not appear to impair the efficacy of this test. A strong solution of hydrate of soda in water, used in a similar manner, affords an excellent test for manganese, little inferior in delicacy to potash, but the latter is shown to be preferable.

Carbonate of soda has long been regarded as one of the most delicate tests of manganese, especially if aided by a little nitrate or chlorate of potash, but that carbonate is much inferior as a test for manganese to potash or soda, requiring a far higher temperature to form the manganate of soda, and the aid of oxidizing substances, as nitre and chlorate of potash, which are quite unnecessary with those alkalies. Borax, too, in point of delicacy is not to be compared with the fixed alkalies as a test for manganese.

The author is of opinion that the fixed alkalies in solution and silver foil will form a valuable addition to the agents employed by the mineralogist and chemist in the examination of minerals, ores, &c.

2. *Sulphur*.—If a little flowers of sulphur be mixed with about its own bulk of the common peroxide of manganese, and exposed on a slip of platinum foil to a red heat, sesquioxide, sulphuret and sulphate of manganese will be formed, and by continuing the heat for a short time, an additional quantity of the sulphate will be produced from the sulphuret. On treating the mass with water and filtering the fluid, a solution of sulphate of manganese will be obtained which will yield a white precipitate with the ferrocyanide of potassium, without a trace of iron.

Similar experiments may be made with any manganese ores, or with substances known or suspected to contain manganese. The quantity of materials operated on may be increased or diminished at pleasure; but if increased, the heat should be continued a little longer, to decompose any remaining sulphuret, and thus add to the quantity of sulphate formed. In the same way manganese was detected in some minerals in which it was known to exist, and in others in which it had not been previously found; likewise in soils and subsoils, in the ashes of coal and peat, in a number of pigments,

and also in the ashes of different fabrics partially dyed brown by manganese.

Sulphate of manganese is formed, with sulphuret, when sulphurous acid gas is made by heating a mixture of peroxide of manganese and flowers of sulphur, even in close vessels. The sulphate may also be more readily obtained, in quantity, by simply boiling a solution of common green vitriol in water for about a quarter of an hour or upwards, in contact with an excess of sesquioxide of manganese in fine powder, till the solution affords a white precipitate with ferrocyanide of potassium.

Chloride of manganese may also be formed in a similar manner by boiling an aqueous solution of protochloride of iron with an excess of sesquioxide of manganese, or it may be made with greater facility by dissolving this oxide in the common muriatic acid of commerce, taking care that the oxide be present in excess.

The brown sesquioxide of manganese may be made, not only by means of sulphur, but more readily and better by mixing the common peroxide with about one-third of its weight of peat mould, sawdust or starch, and exposure to a red heat in an open crucible with occasional stirring for about a quarter of an hour, or until the oxide acquires a uniform brown colour.

The sulphate and chloride of manganese being extensively used in dyeing, calico-printing and other arts, and in making the compounds of manganese, the simple means stated of forming those salts, free from iron (it is presumed), are material improvements on the circuitous methods hitherto adopted.

PATENT.

Patent granted to T. Richardson, *for Improvements in the Manufacture of certain Salts of Magnesia and a Red Colouring Matter.*

This invention consists in diffusing impure carbonate or hydrate of magnesia in water, and passing carbonic acid, obtained from coke or other sources, through the same. After allowing the impurities to subside, the clear supernatant liquid is drawn off and boiled, or otherwise treated, to obtain the ordinary carbonate of magnesia. And this invention also consists in heating sulphate of iron, or impure sulphate of magnesia containing sulphate of iron, with ground fluor spar, for the purpose of obtaining colouring matter and sulphate of magnesia.

The impure hydrate of magnesia, which is a waste product in what is known as Ward's process of carbonating soda ash, is said to be especially adapted for the manufacture of carbonate of magnesia by this process; but any other impure hydrate or carbonate of magnesia free from lime, or nearly so, such as magnesite, may be employed.

In treating any of these forms of magnesia, they are diffused through water, so as to form a cream- or milk-like liquid, which is run into a large soda-water machine, and carbonic acid is pumped

thereon, in the same manner as when soda-water is being made. Or a wooden box, divided into cells, by partitions running from the top and bottom alternately, is partially filled with this milk-like liquid; and by means of a steam-jet or air-pump, worked by suitable machinery, a stream of carbonic acid is drawn through the whole series of compartments from a furnace filled with coke or charcoal. When the liquid becomes saturated with bicarbonate of magnesia, or stands at 5° to 11° on Twaddell's hydrometer, it is drawn off, and after standing about an hour a small quantity of a cream of magnesite is gradually added, which carries down all oxide of iron and other impurities, leaving a clear pure solution of bicarbonate of magnesia. This solution is heated to expel the excess of carbonic acid. The carbonate then precipitates, and is collected and treated in the usual way; or a quantity of pure magnesia, in suspension in water, is added until the whole is precipitated as carbonate of magnesia.

The furnace employed for producing carbonic acid is filled with coke or charcoal, and is supplied with air through an opening at the bottom, and another higher up, on a level with the top of the fuel. The air may be drawn through by means of a jet of steam, or otherwise, or forced forwards by a blowing-cylinder or blast-fan, so regulated by valves or dampers that the supply of air entering at the upper opening shall be a little more than sufficient to convert all the carbonic oxide into carbonic acid, so as to œconomize the fuel and render the action of the gas more energetic on the milk of magnesia. Carbonic acid, obtained from any other source, answers equally well.

At present, in some manufactories, the impure sulphate of magnesia is calcined at a high temperature, in order to convert the iron and manganese into insoluble oxides. This operation is attended with considerable loss of sulphate of magnesia, even with the addition of magnesia to the impure Epsoms previous to calcination. To obviate this loss, 1 part of fluor spar for every 4 parts of the sulphates of iron or manganese present in the impure Epsoms is employed, together with the ordinary quantity of magnesia; and this mixture is calcined at a very low temperature. A double decomposition ensues between the metallic sulphates and the fluor spar, while the metals are rapidly peroxidized and rendered insoluble. The calcined materials are lixiviated, and treated in the usual way for obtaining pure Epsom salts, while the metallic oxides may be employed as a colouring material. Fluor spar may also be calcined with the sulphate of iron in the manufacture of Venetian red. The copperas and fluor spar are mixed in the same proportions as are already named; and so much less gypsum is used as to correspond with that produced from the fluor spar during the operation, the other materials of the batch remaining the same. The operation is conducted in precisely the same manner as at present; but the oxidation is found so much more rapid and perfect, that one furnace turns out as much crude Venetian red as three without the use of the fluor spar.—Sealed June 14th, 1853.

THE CHEMICAL GAZETTE.

No. CCLXXV.—April 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Creosote and its Products of Decomposition.
By M. VON GORUP-BESANEZ.

IN his introduction the author proves that creosote is not to be regarded, as has been done more and more of late, as identical with hydrate of phenyle. This observation refers especially to Gmelin's mode of treating this subject in his 'Manual.' At the same time the author shows that mistakes and uncertainties with regard to creosote are especially caused by the circumstance, that the substance sold as creosote consists sometimes of certain products of the distillation of coal-tar, and then of course contains hydrate of phenyle, and sometimes of products obtained from wood-tar, which are quite different from the preceding.

The creosote employed by the author in the following experiments was obtained from Batka of Prague; according to Prof. Lerch, it is manufactured at Dobriss in Bohemia, and Blansko in Moravia, from beech-wood tar, in accordance with the directions of its discoverer, Reichenbach.

This creosote is an oily, strongly-refractive fluid, of a pale yellowish colour, and a peculiar, penetrating, disagreeable, smoky odour, quite different from that of phenylic acid. It had a sharp burning taste, produced a white spot on the mucous membrane of the tongue, and completely stopped bleeding by coagulating the albumen of the blood. It was completely soluble in alcohol and æther, but sparingly in water; nevertheless water shaken with it acquired the taste, smell, and even the reactions of creosote. It entirely dissolved in sulphuret of carbon, but only partially in acetic acid, even after long boiling. It was also soluble in watery ammonia, acquiring some colour; but all the ammonia was driven off on the water-bath. Muriatic acid produced no change in it; in concentrated sulphuric acid, on the contrary, it was entirely dissolved, and acquired a violet-purple colour. A chip of deal, moistened with muriatic acid and dipped into it, did not exhibit the least trace of a blue or violet colour; nor did the addition of chloride of iron, free of acid, produce any trace of that blue-violet colour which is caused by this reagent even in very dilute solutions of phenylic acid. It could not be obtained crystallized, although the

author repeatedly exposed the perfectly anhydrous substance to very low temperatures. The specific gravity of the crude product varied between 1·046 and 1·049.

Boiling soon showed that this creosote is a mixture of different substances. It began to boil at 194° F., and the boiling-point then rose to 421° F.

The author now separated, by fractional distillation, from the substance purchased as creosote, the body the boiling-point of which lay between 398° and 406° F. This body constitutes the greater portion of the crude creosote, and the thermometer remains stationary for some time between these points.

For this substance the author retains the name of creosote. It is a colourless, oily, strongly refractive fluid, of a peculiar, penetrating, smoky odour, and a pungent burning taste; its specific gravity is 1·040 at 52°·7 F.; it is not crystallizable, but remains fluid at very low temperatures; it is but sparingly soluble in water, but dissolves in alcohol and æther in all proportions. In ordinary acetic acid it is only partially dissolved; it dissolves sulphur and coagulates albumen. In a dose of from 5 to 10 drops, it destroys animals in a few minutes, producing convulsions. It preserves flesh and animal substances generally. Ammonia dissolves creosote, even in the cold. If the ammoniacal solution be evaporated on the water-bath, all the ammonia is driven off. If ammoniacal gas be passed into an alcoholic solution of creosote until saturation, and then followed by sulphurous acid gas, a substance is thrown down in white shining crystals, which retains creosote obstinately, although only mechanically; it is bisulphite of ammonia, with 16 equivs. of water; if sulphuretted hydrogen gas be passed into the ammoniacal solution, bihydrosulphate of ammonia is thrown down; if creosote saturated with ammonia be mixed with alcohol, and sulphuretted hydrogen be then added, yellow crystals are soon formed in the fluid, which from their properties appear to be carbosulphide of ammonium. Creosote is also dissolved by hydrate of potash; the solution, after standing for some time, becomes brownish; when heated with a watery solution of potash, all the creosote is driven off, apparently unchanged. But if creosote be distilled with an alcoholic solution of potash, partial decomposition takes place, and an aromatic oil goes over with the alcohol. Fusing caustic potash decomposes creosote; caustic lime also produces decomposition.

Perchloride of iron produces no change when added to creosote. Nitrate of silver, when heated with it, is reduced, with formation of a beautiful mirror of silver. When creosote is dropped upon freshly precipitated oxide of silver, it produces sufficient heat to cause ignition and explosion. In this case, together with reduced silver, oxalate of silver is produced. Salts of gold, platinum, peroxide of mercury, as well as permanganates, are also reduced by creosote. Concentrated sulphuric acid mixes with creosote, producing a slight heating of the fluid, which acquires a fine purple-violet colour. If this be neutralized with carbonate of baryta, heated to boiling and filtered, a baryta compound is dissolved in the filtrate, which how-

ever becomes decomposed during evaporation on the water-bath, or even at a temperature of 86°–104° F.

Nitric acid, whether concentrated or diluted, resinifies creosote, and brown uncrystallizable products are obtained. Nitrosulphuric acid acts upon it very violently, and a small quantity of a yellowish-white explosive compound is obtained. Chlorine gas acts upon it, with formation of muriatic acid; the substance first acquires a brown, and afterwards a purple-red colour. It is readily decomposed by chlorine; but the author could not obtain a crystallizable chlorinated compound.

Iodine is dissolved by creosote, forming a brown fluid; bromine is also dissolved in considerable quantity. Muriatic acid and chlorate of potash furnish crystallized products of decomposition containing chlorine.

Peroxide of manganese and sulphuric acid, and also chromate of potash and sulphuric acid, produce resinization, with formation of small quantities of a light aromatic oil, and perhaps of formic acid. Peroxide of lead does not act perceptibly upon the acetic acid solution of creosote, nor does it produce any more effect when added to creosote by itself. A chip of deal or fir-wood, moistened with muriatic acid, then dried and passed through creosote, does not acquire the least violet or blue colour. The analyses of the creosote with the boiling-point above given are as follows:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C	75·32	75·72	75·54	74·76	75·82	75·02	74·78	74·68
H	7·84	7·94	7·85	7·95	7·98	7·95	7·98	7·84
O	16·84	16·34	16·61	17·29	16·30	17·03	17·24	17·48

From the preceding the author concludes,—1st, that the creosote under investigation is not identical with hydrate of phenyle; 2nd, that it is not a chemically-definite compound. Combinations with lead and oxide of silver led to no fixed formula.

The author obtained more favourable results by treating creosote with muriatic acid and chlorate of potash. By this treatment the creosote undergoes a change, first becoming brown, then thick and tough and of a red colour, and settling to the bottom. After it has been exposed to this treatment for several days, a mass is obtained, which on cooling is plaster-like and filled with yellow scaly crystals. This mass is repeatedly treated with cold alcohol until the latter no longer acquires a colour; in this manner the yellow scales are left behind, and these are purified by recrystallization from boiling alcohol. To this substance the author gives the name of

Hexachloroxylone.—Its composition is $C^{26}\,H^{6}\,Cl^{6}\,O^{6}$. It appears in beautiful golden-yellow scales, forming rhombic tables with acute angles of about 21°–25°; it is idioelectrical, and may be triturated into a pale yellow powder, of a slightly aromatic odour. If the crystals be heated to 248° F., they begin to sublime, during which the phænomenon of iridescence may be witnessed in great beauty. Sublimation takes place best between 356° and 374° F.; a very small carbonaceous residue is left. When it is too rapidly and strongly

heated, decomposition takes place; the compound becomes brown, and needles and scales of a copper-red colour are sublimed. In water the substance is insoluble, or nearly so. When it is boiled for a considerable time in water, the latter acquires after standing a pale cobalt-red colour; but on evaporation a mere trace of a carbonaceous residue is left. It is also very sparingly soluble in cold alcohol, but dissolves in boiling alcohol of spec. grav. 0·857, forming a yellow solution; it is again deposited, however, on the cooling of the solution. 1 part of it requires about 171 parts of boiling alcohol for its solution. It is readily soluble in æther. It is dissolved by acetic acid with the assistance of heat, but is again precipitated on the cooling of the solution. It is not attacked by muriatic acid; but concentrated sulphuric acid decomposes it even in the cold, and still more rapidly when aided by heat. Hot nitric acid dissolves it without change, but it separates again on cooling. Solution of potash dissolves the crystals with a reddish-brown colour; no crystals separate from the solution even after long standing; after evaporation in a gentle heat, chloride of potassium and an amorphous resinous body remain. If any acid be added to the alkaline solution, an amorphous brownish precipitate is thrown down. Ammonia behaves in exactly the same manner. On analyses it gave numbers which agree in some degree with the composition of a mixture of equal equivalents of chloranile and of Städeler's bichloroquinone; but the crystals appeared homogeneous under the microscope; and the author also concludes, from the properties of the substance, that it is a definite compound. Analyses:—

Carbon	36·78	36·65	36·78	36·69	26	= 156	36·88
Hydrogen	1·59	1·54	1·51	1·53	6	6	1·42
Chlorine.....	..	..	50·62	50·53	6	213	50·35
Oxygen	..	..	..	..	6	48	11·35

When hexachloroxylone is treated to saturation with sulphurous acid gas, and left standing for twenty-four hours in a closed vessel, it is converted into a brownish-white substance, which forms four-sided prisms. These are separated by filtration and washed. The filtered fluids also contain a body, which remains after evaporation in an amorphous state, and of a fine violet colour. This substance dissolves in a mixture of alcohol and æther, forming a fluid of a pale yellowish colour, which soon becomes darker and brownish-yellow; on the sides of the vessel, needle-like crystals of an inch in length are then formed, which appear dark violet by transmitted, blackish-green by reflected light; from the mother-liquor brownish-white needles afterwards crystallize. These consist of a substance which is produced from the preceding compound by the accession of 4 equivs. of hydrogen; the author therefore calls it

Hexachlorhydroxylone.—Its composition is $C^{26}\,H^{10}\,Cl^{6}\,O^{6}$. The brownish-white crystals of this compound are soluble in cold strong alcohol and in æther; they dissolve in dilute alcohol by boiling, but are again deposited from it on cooling; in water they are but sparingly soluble; water boiled with them acquires a dingy violet

colour in time. If the crystals be dissolved in strong alcohol and æther, a portion of them is apparently converted into another violet compound. If hexachlorhydroxylone be boiled for a considerable time with constantly renewed water, the water takes up a small quantity of it, but lets it fall again even during filtration at a boiling heat; during this, the fluid, which is at first only of a pale yellow colour, acquires a distinct cobalt-red, and afterwards a dingy violet colour; after some time acicular crystals are formed on the surface, which are blackish-green by reflected, dark violet by transmitted light. They probably consist of the compound to be mentioned hereafter. Acetic acid also dissolves hexachlorhydroxylone with the aid of heat, and that deposited on cooling contains numerous intermixed blackish-red needles; if the treatment with acetic acid be repeated, a portion is always changed in this manner. The compound may be almost completely precipitated from its cold alcoholic solution by means of water. At 356° F. it sublimes without previous fusion, forming acicular crystals of from 1 to 1½ line in length, and leaving a very small carbonaceous residue.

Dilute solutions of potash and ammonia give a chrome-green colour to the crystals; they then dissolve into a dingy green fluid, which soon passes to brownish-red. From the solution in potash muriatic acid throws down a brownish-yellow, resinous, amorphous body. Concentrated sulphuric acid does not act upon hexachlorhydroxylone in the cold; but with the assistance of heat this reagent produces a rapid decomposition, with a dark brown colour. Concentrated nitric acid, after acting upon it for a considerable time, converts it into golden-yellow rhombic laminæ. A neutral solution of perchloride of iron also converts it into yellow scales and laminæ. If an alcoholic solution of hexachlorhydroxylone be treated with nitrate of silver, a mirror of metallic silver is formed; and the filtrate, when evaporated, furnishes dark violet crystals. Hypochlorite of soda converts it into yellow laminæ. Analysis:—

Carbon	36·86	36·92	37·02	26 =	156	36·53
Hydrogen ..	2·23	2·39	2·38	10	10	2·34
Chlorine	..	..	..	6	213	49·88
Oxygen	..	..	..	6	48	11·25

Violet Compound, probably of the same composition. Even in solution in a mixture of alcohol and æther, and still more when boiled, the preceding substance becomes converted into a violet compound. The same thing takes place when it is treated with nitrate of silver and acetic acid.

This compound forms prismatic crystals of a dark red or nearly black colour, which appear dark violet under the microscope, and by reflected light of a blackish-green; they are inodorous, and have a caustic taste; they are insoluble in cold water, and dissolve very sparingly in boiling water, to which they give a yellow colour; they dissolve in alcohol and æther, but during solution a portion of the compound is always converted into yellow rhombic tables; hot acetic acid also dissolves them, but they crystallize from this solu-

tion on cooling, and are partially converted into brownish-white needles. Potash and ammonia dissolve the violet compound with the assistance of heat, forming a reddish-brown solution; the crystals first become dingy green, then pale green, and finally pale yellow; acids generally produce amorphous precipitates in these solutions. Concentrated sulphuric acid dissolves them with a brownish-red colour when heated; if the solution in sulphuric acid be diluted with much water, a powder of a violet-red colour falls to the bottom; this appears amorphous under the microscope. The violet compound is only dissolved with difficulty by boiling concentrated nitric acid; muriatic acid does not touch it. Nitrate of silver produces a white flocculent precipitate in its alcoholic solution. Hypochlorite of soda produces no change. If a small quantity of strong alcohol be poured over the crystals, they become converted into yellow rhombic prisms during the spontaneous evaporation of the spirit.

From these properties the author concludes that the violet hexachlorhydroxylone corresponds with Städeler's violet bichlorhydroquinone. It would then be possible that the yellow compound into which the violet crystals are converted by alcohol may represent Städeler's yellow bichlorhydroquinone, if it be not hexachlorhydroxylone again.

From these analogies the author then comes to the conclusion, that just as when kinic acid is treated with chlorine, quinone, $C^{12} H^4 O^4$, becomes converted into chloroquinones with 1–3 atoms of chlorine instead of hydrogen, there are also several chloroxylones; so that he supposes hypothetically that there is a xylone, $C^{26} H^{12} O^6$, in which the hydrogen may be replaced by chlorine. It appeared, in fact, that several compounds were still contained in the fluid filtered from the yellow scales.

This fluid, after standing some hours, deposits a sediment, in which the microscope shows resinous flakes, crystalline scales, needles and oleaginous drops. Strong alcohol dissolves all except the scales, which were not in sufficient quantity for analysis. The solution obtained by the treatment of the mass of crystals with very dilute boiling alcohol also deposited on cooling a flocculent granular sediment, in which the microscope likewise showed oleaginous drops, resin, transparent tabular scales, and laminæ resembling cholesterine. This was repeatedly washed on the filter with cold strong alcohol, and then repeatedly recrystallized from boiling dilute alcohol. This compound now formed tolerably large, beautiful, glassy, four-sided rhombic tables, of a pale golden-yellow colour, which were distinguished from hexachloroxylone by their general appearance. For analysis this substance was sublimed; it was thus obtained in beautiful, extremely thin, flexible laminæ, which appeared iridescent by transmitted light. This compound is

Pentachloroxylone, $C^{26} H^7 Cl^5 O^6$.—It is insoluble in water, but soluble in boiling dilute alcohol, from which it may be completely precipitated by water. A portion of it is separated even during cooling. It is soluble in æther in all proportions. It is also

soluble in boiling acetic acid, although apparently with more difficulty than hexachloroxylone. Nitric acid dissolves it only after long boiling; it dissolves in sulphuric acid with a brownish-red colour.

Cold ammonia slightly attacks the crystals; when heated, it dissolves them with a violet colour; potash also acts upon them with difficulty when cold, but dissolves them when heated, forming a blackish-brown solution. Nothing is separated from the solution in potash after standing a considerable time. The crystals sublime at from 329° to 356° F. without fusing. Analysis gave—

Carbon	39·79	26 =	156·0	40·15
Hydrogen	1·91	7	7·0	1·80
Chlorine.....	..	5	177·5	45·68
Oxygen	..	6	48·0	12·37

Oxide of Silver and Creosote.—When creosote is dropped upon oxide of silver, a very violent action takes place, with production of heat, ignition and explosion. On the other hand, when oxide of silver is added to an excess of creosote, a mass which is constantly becoming thicker is obtained, which finally acquires a purple-red colour, and a thick syrup-like consistence. The silver lies at the bottom, partly in the metallic form and partly as oxalate.

These products are not pure or definable bodies. Amongst them the author distinguishes α- and β-resin. The mass, except the silver and oxalate of silver, is soluble in strong boiling alcohol; this deposits one resin on cooling, but retains the other in solution.

α-Resin is that which is soluble in cold alcohol. It is a brown mass (liver-coloured when powdered), strongly idioelectrical, with an aromatic, and by no means unpleasant odour. It fuses between 131° and 141° F., and is insoluble in water, but readily soluble in alcohol and æther. It is insoluble in ammonia and alkaline carbonates, but soluble in caustic potash; during solution the fluid first acquires a dingy green colour, then becomes dark violet, and lastly brownish-green. When the alkaline solution is supersaturated with acids, the fluid first of all acquires a pale vermilion colour, and then deposits the resin. The separation of the resin from its alcoholic solution by means of water is greatly assisted by the addition of a small quantity of chloride of sodium or sulphate of magnesia. The alcoholic solution of the resin has a weak acid reaction. When heated, it becomes inflated, takes fire, and burns without residue. Lastly, its alcoholic solution is precipitated by acetate of lead, without the addition of ammonia. Its analysis gave—

Carbon.....	72·49	24 =	144	72·72
Hydrogen.....	6·93	14	14	7·07
Oxygen.....	20·58	5	40	20·21

The lead compound of this α-resin is of a silvery colour, and insoluble in water and æther. Its analysis gave—

Carbon	48·28	..	..	24 =	144	46·45
Hydrogen ..	4·36	..	..	14	14	4·51
Oxygen	..	..	..	5	40	12·91
Oxide of lead	..	37·00	36·37	1	112	36·13

The β-Resin is that which is insoluble in cold alcohol. Its analysis gave—

	I.	II.
Carbon	75·52	76·23
Hydrogen	7·09	6·65
Oxygen	17·39	17·12

which nearly corresponds to the formula $C^{24} H^{13} O^4$.

On distillation of creosote with strong bases, compounds are obtained, some of which may be isolated, and appear to have a constant composition. If lime be employed for this purpose, the fluid, when heated above 204° F., begins to boil; at 212° a milky fluid goes over. The thermometer then rises, and at 356°–374° F. a fluid of an aromatic odour and lighter than water passes rapidly over; but when the thermometer has risen to 397° F., there passes an oil, which distils in æther-like bands, and is heavier than water. Almost the whole of this goes over between 397° and 406°. It was deprived of water over chloride of calcium, and then distilled, when a small quantity of a light oil passed over at 342° F., which possessed the properties of capnomor.

The oil which passed over between 397° and 406° F., when rectified, gave on analysis—

	I.	II.
Carbon	78·74	78·55
Hydrogen	8·54	8·61
Oxygen	11·72	12·84

This is almost the same composition as that of the oil obtained by Völckel in the dry distillation of wood at 221°–230° F.

To determine whether a sample of commercial creosote is, or contains, carbolic acid, the boiling-point, according to the author's experience, is generally sufficient. It is also safe to test the product with perchloride of iron and acetic acid. When carbolic acid is present, perchloride of iron always produces a violet-blue colour, and afterwards a whitish turbidity; acetic acid completely dissolves carbolic acid with the assistance of a gentle heat. Creosote prepared from beech-wood tar is not altered by perchloride of iron, and is only partially dissolved by hot acetic acid of ordinary concentration. In conclusion, the author shows that it still remains to be ascertained whether phenylic acid occurs generally in wood-tar.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 257.

On the Behaviour of Sulphuret of Arsenic with Alkaline Carbonates. *By* H. Rose.

When a mixture of sulphuret of arsenic, AsS^3, with an alkaline carbonate is fused in a glass tube, a mirror of metallic arsenic is obtained; the fused mass contains a sulpho-salt of the highest sulphuret of arsenic, AsS^5, with the sulphuret of the alkaline metal and arseniate of the alkali. In this case 5 atoms of sulphuret of arsenic, AsS^3, are converted, with separation of 2 atoms of metallic arsenic,

into 3 atoms of AsS^5, which form with the alkali the above mentioned sulpho-salt and the alkaline arseniate.

If the sulphuret of arsenic, AsS^3, be fused with the alkaline carbonate in a stream of hydrogen gas, a strong mirror of arsenic is obtained; but the mixture does not lose all its arsenic, as is pretty generally supposed; for the sulpho-salt formed with the highest sulphuret of arsenic, AsS^5, and the sulphuret of the alkaline metal is not decomposed by heating in a stream of hydrogen gas, but only the alkaline arseniate, which is formed at the same time, and which is converted into hydrate of the alkali whilst metallic arsenic is expelled, simultaneously with that resulting from the conversion of AsS^3 into AsS^5. When the alkaline arseniate is reduced by hydrogen gas, it is first of all converted into arsenite, which is generally found in the fused mass.

When the sulphuret, AsS^5, is fused with an alkaline carbonate, no sublimate of metallic arsenic is obtained. The sulpho-salt of the highest sulphuret, AsS^5, with the sulphuret of the alkaline metal is produced without any separation of arsenic. The same result is obtained when the sulphuret, AsS^5, is fused in a glass retort, or in a stream of hydrogen gas with a mixture of an alkaline carbonate and an excess of sulphur. Only the sulpho-salt of the highest sulphuret is produced, and nothing is volatilized but the excess of sulphur.

But if the sulphuret, AsS^5, be fused with an alkaline carbonate in a stream of hydrogen gas, a spot of metallic arsenic is obtained. Whilst the sulpho-salt produced by the fusion remains undecomposed in the stream of hydrogen, the alkaline arseniate is reduced, and metallic arsenic sublimes. The latter is also reduced by powdered charcoal when this is added to the mixture of AsS^5 and alkaline carbonate, and the whole melted in a retort.—*Monatsbericht der Akad. der Wiss. zu Berlin*, 1853, p. 713.

On the Yellow Colouring Matter of the Bark of the Root of the Bird-Cherry (Rhamnus frangula). *By* L. A. Buchner.

A peculiar yellow colouring matter is contained in the bark of the root of the bird-cherry; it may be extracted by æther. From the alcoholic extract of the same bark, æther extracts this body mixed with fat. If the ætherial alcoholic extract be put into Mohr's apparatus for obtaining benzoic acid, it is obtained in yellow crystals. The author describes this new colouring matter as—

Rhamnoxanthine.—It is a tasteless non-azotized body. It has not yet been analysed. When heated, it leaves a cinder; but a portion of it is volatilized undecomposed in yellow vapours, which first condense in drops, and afterwards solidify. It dissolves in hot water, forming a fluid of a slight yellow colour, from which the greater part of the substance separates on cooling, as it is but sparingly soluble in cold water. Paper coloured with this substance is very soon bleached by exposure to light. Rhamnoxanthine is dissolved by ammonia and the fixed alkalies with a purple-red colour, a pro-

perty which it has in common with some other yellow colouring matters, and especially with chrysophanic acid, from which however it differs in many respects. Thus, amongst other things, it is distinguished from chrysophanic acid by its greater volatility and much greater solubility in alcohol and æther. When its alkaline solution is saturated with an acid, the substance is again separated with a pale yellow colour. It dissolves in concentrated sulphuric acid, forming a purple or blood-red fluid, from which dilution with water throws down a pale yellow precipitate, which is soluble with a purple colour in alkalies. The bark of the stem and the seeds of *Rhamnus frangula* and *R. catharticus* also contain the colouring matter. But the unripe berries of the latter plant and those of *R. infectoria*, the so-called "yellow berries" or "Avignon grains," which are employed in dyeing yellow, contain no rhamnoxanthine.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 219.

On some Compounds of the Peroxide of Mercury with Allantoin. *By* Dr. H. Limpricht.

When a watery solution of allantoin is boiled with an excess of peroxide of mercury, a portion of the latter is dissolved, and the boiling solution then contains two compounds of peroxide of mercury with allantoin; one of these separates on the cooling of the fluid, and the other is obtained by the evaporation of the mother-liquor.

The first compound, consisting of $3(C^8 H^5 N^4 O^5) 5HgO$, is a white powder, which does not appear crystalline under a magnifying power of 500 diameters; it is insoluble in alcohol and cold water, dissolves sparingly in hot water, and readily in mineral acids. When heated, it fuses and becomes inflated. Analysis:—

C	14·28	14·40	14·12	..	..	24	=144	14·51
H	1·65	1·59	1·48	..	..	15	15	1·51
N	..	..	..	..	..	12	168	16·93
O	..	..	..	..	..	15	120	12·09
HgO	54·84	54·19	55·30	55·26	54·57	5	545	54·93

The second compound, $5(C^8 H^5 N^4 O^5) 3HgO$, which is obtained by the evaporation of the mother-liquor of the preceding on the water-bath, is of a turpentine-like consistence when reduced to a small volume; when dried, it forms a brittle glassy mass, which swells up when water is poured over it. It becomes black at 212° F. For analysis it was dried at 140° F. It furnished:—

Carbon	21·23	40	= 240	22·39
Hydrogen	2·74	25	25	2·23
Nitrogen	..	20	280	26·11
Oxygen	..	25	200	18·65
Oxide of mercury..	29·06	3	327	30·50

Another compound, $3(C^8 H^5 N^4 O^5) 4HgO$, is formed when water is poured over the preceding turpentine-like mass. It becomes black when heated above 212° F. Analysis:—

Carbon.....	16·12	..	24 = 144		16·30
Hydrogen	1·75	..	15	15	1·69
Nitrogen	..	..	12	168	19·02
Oxygen	..	..	15	120	13·69
Oxide of mercury..	48·66	49·6	4	436	49·30

A compound of the formula $2(C^8 H^5 N^4 O^5) 5HgO$ was obtained by the author by adding nitrate of mercury to the solution of allantoin; this formed a voluminous non-crystalline precipitate. Bichloride of mercury produced no precipitate. Analysis:—

Carbon	11·14	11·35	11·29	..	16 =	96	11·38
Hydrogen	1·07	1·03	1·14	..	10	10	1·18
Nitrogen	..	..	..	12·95	8	112	13·28
Oxygen	..	..	..	..	10	80	9·48
Oxide of mercury	65·17	64·66	63·97	..	5	545	64·65

It appears from the preceding that allantoin behaves exactly like urea; it may therefore be determined by the method proposed by Liebig for urea. At the same time it must, of course, be borne in mind that urea cannot be determined by this process in fluids containing allantoin.

The above compound is always produced when a cold saturated or concentrated watery solution of allantoin is mixed with the solution of pernitrate of mercury employed by Liebig in the determination of urea. From the composition of the precipitate, it appears that 100 milligrms. of allantoin require for their precipitation 172 milligrms. of peroxide of mercury; 10 cub. centims. of the solution of pernitrate of mercury containing 772 milligrms. of peroxide of mercury, will consequently precipitate 448 milligrms. of allantoin. But to obtain a distinct yellow precipitate on the addition of carbonate of soda, an excess of peroxide of mercury in the fluid is necessary; and as, in consequence of the slight solubility of allantoin in water, we are compelled to employ very dilute solutions of it, the excess of oxide of mercury in the reagent must always be still more considerable than in the determination of urea. According to some experiments, 10 cub. centims. of the mercurial solution indicate 360–365 milligrms. of allantoin; each cubic centimetre of the mercurial solution therefore contains an excess of 14·5 milligrms. of peroxide of mercury.

A compound with oxide of copper, perhaps $3(C^8 H^5 N^4 O^5) CuO$, is formed when a solution of allantoin is boiled with hydrated oxide of copper; the solution is blue, the crystallized compound green. It contains 7·23–7·36 per cent. of oxide of copper; the above formula requires 8·2 per cent.

By boiling solutions of allantoin with other metallic oxides, the author also obtained the following compounds:—

One with oxide of lead, $2(C^8 H^5 N^4 O^5) 3PbO$, was deposited in crusts, which, when dried at 212°, contained 52·5 and 52·8 per cent. of oxide of lead.

Another with oxide of zinc, perhaps $C^8 H^5 N^4 O^5, 2ZnO$. From the hot filtered solution allantoin crystallized first of all; a syrup-

like mother-liquor remained, which was precipitated and washed with absolute alcohol. The precipitate, 0·093 grm., when dried at 212° F., furnished 36·5 per cent. of oxide of zinc. The above formula requires 35 per cent. ZnO.

And one with oxide of cadmium, $C^8 H^5 N^4 O^5$, CdO, which constitutes a syrup-like mass, solidifying on the addition of alcohol into a white crystalline powder; it contains 28·04 per cent. of oxide of cadmium. The formula $C^8 H^5 N^4 O^5$, CdO requires 30·0 per cent. of oxide of cadmium. The powder thrown down by alcohol is not completely resoluble in hot water; the residue is a compound containing more oxide of cadmium.

Fermentation of Allantoin.—On the preceding memoir Wöhler observes, that when yeast is added to solution of allantoin, the mixture becomes ammoniacal within four days. It then contains urea, oxalic acid, carbonic acid, ammonia, and an acid, obtained in the form of an acid syrup, but which has not yet been more closely investigated.—*Ann. der Chem. und Pharm.*, lxxxviii. p. 94.

On the Deodorizing and Disinfecting Properties of Charcoal, with the description of a Charcoal Respirator for purifying the Air by Filtration. *By* John Stenhouse, LL.D., F.R.S.

The powerful effects of freshly-burned wood-charcoal, especially when coarsely powdered, in absorbing gases and vapours, have been long known. Hence the limited extent to which charcoal has been occasionally employed to sweeten fœtid water and animal substances in the incipient stages of putrefaction. Sufficient attention has not, I think, however, been hitherto bestowed on a second and still more important effect which charcoal exerts upon those complex products of decomposition, viz. that of rapidly oxidizing them and resolving them into the simplest combinations they are capable of forming.

When coals or wood are burned with an inadequate supply of air, a variable amount of intermediate or secondary products is generated, constituting what are called soot and smoke; when, on the other hand, the combustion of the fuel is conducted with an adequate supply of oxygen and a sufficiently high temperature, carbonic acid, water, ammonia, with perhaps a little nitric acid, are almost the sole products.

The putrefaction of animal and vegetable substances is likewise in general a process of imperfect oxidation. Hence, under ordinary circumstances, when this is the case, a variety of more or less complex secondary products is formed, which usually possess very disagreeable odours, and exert exceedingly injurious effects upon the animal œconomy. To these substances the general name of *miasmata* has been given. Not much is known of their nature; but they are believed to be heavy, complex, nitrogenated vapours, which are decomposed by oxygen, chlorine, sulphurous acid, nitric acid, and other disinfecting agents.

My attention was particularly drawn to the importance of charcoal as a disinfecting agent by my friend John Turnbull, Esq., of

Glasgow, the well-known extensive chemical manufacturer. Mr. Turnbull, about nine months ago, placed the bodies of two dogs in a wooden box, on a layer of charcoal-powder of a few inches in depth, and covered them over with a quantity of the same material. Though the box was quite open, and kept in his laboratory, no effluvium was ever perceptible; and on examining the bodies of the animals at the end of six months, scarcely anything remained of them except their bones. Mr. Turnbull sent me a portion of the charcoal-powder which had been most closely in contact with the bodies of the dogs. I submitted it for examination to one of my pupils, Mr. Turner, who found it contained comparatively little ammonia, not a trace of sulphuretted hydrogen, but very appreciable quantities of nitric and sulphuric acids, with acid phospate of lime.

Mr. Turner subsequently, about three months ago, buried two rats in about 2 inches of charcoal-powder, and a few days afterwards the body of a full-grown cat was similarly treated. Though the bodies of these animals are now in a highly putrid state, not the slightest odour is perceptible in the laboratory.

From this short statement of facts, the utility of charcoal-powder, as a means of preventing noxious effluvia from churchyards and from dead bodies in other situations, such as on board ship, is sufficiently evident. Covering a churchyard to the depth of from 2 to 3 inches with coarsely-powdered charcoal, would effectually prevent any putrid exhalations ever finding their way into the atmosphere. Charcoal-powder also greatly favours the rapid decomposition of the dead bodies with which it is in contact, so that in the course of six or eight months little is left except the bones.

In all the modern systems of chemistry, such, for instance, as the last edition of Turner's 'Elements,' charcoal is described as possessing antiseptic properties, while the very reverse is the fact. Common salt, nitre, corrosive sublimate, arsenious acid, alcohol, camphor, creosote, and most essential oils are certainly antiseptic substances, and therefore retard the decay of animal and vegetable matters. Charcoal, on the contrary, as we have just seen, greatly facilitates the oxidization, and consequently the decomposition, of any organic substances with which it is in contact. It is, therefore, the very opposite of an antiseptic.

The object of the present paper, however, is chiefly an application of the absorbent and oxidizing properties of charcoal, which, so far as I am aware, has never yet been proposed, viz. to employ a new species of respirator, filled with powdered animal charcoal, to absorb and destroy any miasmata or infectious particles present in the air in the case of fever and cholera hospitals, and of districts infected by ague, yellow fever, and similar diseases. I have got such a respirator made by Ferguson and Sons, Smithfield, instrument-makers to St. Bartholomew's Hospital. It fits closely to the lower portion of the face, extending from the chin to within half an inch of the eyes, and projects about an inch on either side of the mouth. It therefore includes the nostrils as well as the mouth.

The frame of the respirator is made of thin sheet copper, but the edges are formed of lead, and are padded and lined with velvet, so that it can be easily made to fit tightly to the face. The powdered charcoal is kept in its place by means of two sheets of fine wire gauze, from a quarter to an eighth of an inch apart. As the body of the apparatus is metallic, it has been electro-plated with silver. Electro-plating the respirator with platinum or gold would certainly be an improvement. There is a small opening closed with a wire-gauze screw, by means of which the respirator can be filled with charcoal or emptied at pleasure. The respirator is kept in its place by an elastic band passing round the back part of the head. I have employed *animal* charcoal as the more porous substance, but I should think wood-charcoal would answer perfectly well*. The object in view is, by filtering the air through such a porous substance as animal charcoal, to intercept the miasmata which may have got mixed with it. These, I think, cannot fail to be absorbed by the pores of the charcoal, where they will be rapidly oxidated and destroyed by the condensed oxygen with which they will be brought into the most intimate contact. The probability of this expectation being realized is greatly strengthened by the results of repeated trials with the respirator on certain noxious and offensive gases, such as ammonia, sulphuretted hydrogen, hydrosulphate of ammonia and chlorine. I have found that air strongly impregnated with these gases, and which could not be respired for any length of time under ordinary circumstances, may be breathed with impunity when the charcoal respirator is worn, the odour of these gases being rendered almost, if not altogether imperceptible. Any other highly porous substance, such for instance as sponge platinum, or pounded pumice-stone, might probably be found to answer perfectly well for filling the respirator; but I have selected charcoal as the cheapest and most easily available material.

While the filtration of water through charcoal powder and other porous substances has been advantageously practised for many centuries, the object in view being to deprive the water of numerous impurities diffused through it, which produce injurious effects on the animal œconomy, it is certainly somewhat remarkable that the very obvious application of a similar proceeding to the lighter fluid in which we live, viz. air, which not unfrequently contains even more noxious impurities floating in it than are usually present in water, should have, up to the present time, been so unaccountably overlooked.

In addition to the precaution of wearing such a respirator as that just described, persons necessitated to live in especially pestiferous districts might have their houses made as air-tight as possible, with the exception of such openings as are necessary to maintain a proper amount of ventilation. By means of these openings the air could be freely admitted through gauze into which the requisite quantity of charcoal had been quilted. The doors of such houses could also

* Since the above was written, I have ascertained by experiment that common wood-charcoal is even more efficacious than animal charcoal.—J. S.

be made double, and be constructed of coarse cloth, likewise containing a thin layer of charcoal powder. As an additional precaution, if it were thought desirable, the walls, floors, and ceilings of houses in very unhealthy districts could be easily lined with mattrasses filled with a couple of inches of charcoal powder. Were these and similar precautions adopted, I confidently anticipate that Europeans will be enabled to reside with comparative impunity in some of the hitherto most pestilential districts of the world.—*Journal of the Society of Arts*, Feb. 24, 1854.

On some Compounds of Oxalic Acid with Metallic Oxides. *By* S. Hausmann *and* J. Löwenthal.

Oxalate of Protoxide of Tin, $3SnO, C^2O^3 + HO$, is the white precipitate which is thrown down by oxalic acid from a solution of chloride of tin. This salt is permanent in the air; it is but sparingly soluble in hot or cold water, insoluble in oxalic acid, difficult of solution in cold dilute acids, but readily soluble in hot muriatic or nitric acid,—in the latter with evolution of slight red fumes. By continued heating of the solution in nitric acid, oxide of tin is separated. The salt is pretty readily soluble in hot solutions of ammoniacal salts, from which it separates again partially on cooling in the form of small crystals. It cannot be freed from all its water by drying at 212°–320° and 356°; from 2 to 3 per cent. adhere to it obstinately. When heated to redness in the absence of air, there remains protoxide of tin with some charcoal. In the first of these analyses, the salt was dried at 212° F., in the second at 320° F. If the water be deducted as non-essential, we get the formula SnO, C^2O^3:—

	I.	II.						
SnO	63·56	63·61	3	63·14	SnO	65·44	1	64·96
C^2O^3	33·64	33·43	3	34·02	C^2O^3	34·51	1	35·04
HO	2·80	2·91	1	2·84				

Oxalate of Protoxide of Tin and Potash, $SnO, KO, 2C^2O^3 + HO$. —Freshly-precipitated oxalate of protoxide of tin is dissolved in a hot concentrated solution of neutral oxalate of potash. Limpid columnar crystals are formed, which are readily soluble in hot water, but less so in cold; alcohol does not dissolve them. Acids separate oxalate of protoxide of tin from the solution. The salt has a remarkably sweet taste, which afterwards becomes sharp; it reddens litmus, and undergoes no change at 212° F., or by exposure to the air. Analysis:—

SnO	34·68	1 =	66·82	34·27
KO	24·35	1	47·20	24·20
C^2O^3	36·30	2	72·00	36·91
HO	4·67	1	9·00	4·62

Oxalate of Protoxide of Tin and Soda resembles the preceding.

Oxalate of Protoxide of Tin and Oxide of Ammonium, $SnO, NH^4O, 2C^2O^3 + HO$.—Oxalate of protoxide of tin is dissolved in

concentrated boiling solution of oxalate of ammonia, and alcohol is added after the cooling of the mixture. The salt forms acicular crystals grouped in a stellate form, which effloresce in the air, and dissolve very readily in water, but not in alcohol; they also have a very sweet taste. The concentrated solution, after long standing, deposits oxalate of protoxide of tin. Analysis:—

SnO	38·00	1 =	66·82	38·44
NH^4O	15·60	1	26·00	14·95
C^2O^3	40·52	2	72·00	41·42
HO	5·88	1	9·00	5·19

Oxalate of Peroxide of Tin. — Freshly-precipitated hydrated peroxide of tin dissolves readily in hot oxalic acid. The solution, whether saturated or not with oxide of tin, becomes blue when exposed to the light of the sun, but loses its colour again in the dark. The salt, obtained in laminæ by the evaporation of the non-saturated solution, loses oxide of tin by recrystallization. The solution, when saturated with oxide of tin, has a somewhat milky appearance, and furnishes no crystals on evaporation, but gives instead a colourless jelly, which dries into gum-like pieces. These, when triturated, furnish a white powder, which is soluble in water; its composition is not constant, as the amount of oxide of tin contained in it varies from 72 to 80 per cent. By treating with small quantities of cold water, the salt constantly becomes more and more basic, more oxalic acid than oxide of tin being dissolved.

Many neutral salts produce precipitates in the solution of peroxide of tin in oxalic acid,—as the nitrates, sulphates and chlorides. Alkalies and alkaline carbonates give white precipitates, which are soluble in water immediately after precipitation, although they become insoluble when they remain any time in contact with the fluid, or when heated with it. Ammonia also produces white precipitates, which are readily soluble both in water and in an excess of ammonia. These separate again from the ammoniacal solution after some time, but are then no longer soluble in ammonia; they still dissolve in water, in which however they become insoluble when they have remained long in contact with the ammoniacal fluid. The precipitates just mentioned, which are soluble in water, dry at 212° F. into gum-like fragments, which are now nearly insoluble in water, which only takes up some oxalic acid and a trace of oxide of tin. When heated to redness, they leave a coal, which when burnt leaves pale yellow oxide of tin. The composition of all appears to be similar. The analysis of those obtained by chloride of ammonium (I.) and by cold nitric acid (II.) gave the formula $6SnO^2, C^2O^3+6HO$:—

	I.	II.			
SnO^2	83·64	83·28	6 =	448·92	83·30
C^2O^3	6·64	6·78	1	36·00	6·68
HO	9·72	9·94	6	54·00	10·02

Oxalate of Protoxide of Manganese, MnO, C^2O^3+2HO, obtained by the decomposition of freshly-precipitated carbonate of protoxide

of manganese with oxalic acid, has the following composition when dried at 212° F.:—

MnO	39·92	1 =	35·57	39·72
C^2O^3	39·20	1	36·00	40·19
HO	20·88	2	18·00	20·09

Oxalate of Copper, CuO, C^2O^3 + HO, was prepared by the precipitation of a solution of sulphate of copper by oxalic acid at 212° F. Very little copper remained in the solution. Analysis:—

CuO	47·77	1 =	40	47·06
C^2O^3	41·74	1	36	42·35
HO	10·49	1	9	10·59

Oxalate of Silver, AgO, C^2O^3, obtained from nitrate of silver by oxalic acid is a white powder, which obstinately retains 2 per cent. of water; if this be deducted, the salt contains:—

AgO	76·83	1 =	116	76·31
C^2O^3	23·17	1	36	23·69

Ann. der Chem. und Pharm., lxxxix. p. 104.

Occurrence of Fumaric Acid in Corydalis bulbosa.

Dr. Wicke has found fumaric acid in the juice of the herb of *Corydalis bulbosa.—Ann. der Chem. und Pharm.*, lxxxvii. p. 225.

On a new Organic Base in the Tissue of the Thymoid Gland.
By E. von Gorup-Besanez.

As much as possible of the substance of the thymoid glands of a calf, freed from fat, was extracted with cold water in accordance with Liebig's method for the investigation of the fluids of flesh. This fluid is strongly acid, and deposits much albumen when boiled. The fluid filtered from this furnishes a considerable precipitate of sulphate and phosphate of baryta when treated with caustic baryta. During evaporation films are formed, consisting of baryta and a substance like caseine, and the residue has a pleasant odour like broth.

No creatine separated from this residue, nor could either creatinine or inosic acid be detected in it. When the syrupous residue was agitated with alcohol and left to stand in a tall glass, a syrup fell to the bottom, and semitransparent verrucose masses were deposited on the sides of the glass; these appeared to the naked eye like crystalline masses, but under the microscope were seen to be composed of granules. They consist of a new base, to which the author gives the name of *thymine*, in reference to the situation in which it occurs. Only 200 milligrms. of this base were obtained from 21 lbs. of fresh glands. It was obtained pure and in a crystalline form by repeated solution in hot alcohol.

The properties of this body, of which the composition is not yet ascertained, are as follows:—

Thymine forms slender snow-white needles, grouped concentrically; it is perfectly inodorous and tasteless. When quickly heated

upon platina foil, it burns with a bluish and not very luminous flame, leaving no residue. When heated in a narrow glass tube closed at the lower end, a white sublimate is deposited immediately in front of the heated spot; and this, when the heat is increased, fuses into a brownish fluid. If the glass tube be allowed to cool at this period, this fluid sets into acicular crystals, which are visible even to the naked eye. When the heat is continued, an odour like that of hydrocyanic acid is produced, and the fumes evolved render reddened litmus-paper blue. Lastly, it is completely burnt, leaving a slight carbonaceous residue.

Thymine is very readily soluble in water; it also dissolves in boiling alcohol of specific gravity 0·848, but is partially deposited again on the cooling of the solution; it is but sparingly soluble in strong cold alcohol; boiling absolute alcohol also dissolves it very sparingly, and æther apparently not at all. In solution of potash it dissolves even when cold, without any evolution of ammonia, nor does this take place when the solution is heated; when triturated with hydrate of lime, with the addition of a few drops of water, no trace of ammonia is evolved. It is also soluble in caustic ammonia. The concentrated watery solution of thymine does not render reddened litmus-paper blue; but if a little thymine be laid upon moistened reddened litmus-paper, a certain amount of blueness, although very little, is produced at the point of contact. Thymine contains no sulphur. Nitrate of silver, bichloride of mercury, and protochloride of zinc produce no precipitates in its concentrated watery solution; on the addition of potash and sulphate of copper no reduction of the oxide of copper is effected, and hydrated oxide is precipitated. Thymine combines with acids and with chloride of platinum, forming crystalline compounds.

Muriate of Thymine was obtained by the solution of the substance in muriatic acid; on the evaporation of the solution, it formed fine acicular crystals; by spontaneous evaporation, it was obtained in short four-sided prisms. The salt is very readily soluble in water; when long exposed to the air, it appears to lose a portion of its acid, and becomes white and opake. Ammonia produces no precipitate in its solution.

Sulphate of Thymine crystallizes in broad, six-sided, transparent prisms, very like those of cystine. This salt also effloresces in the air.

Chloride of Platinum and Thymine forms beautiful yellow granules, which, under the microscope, appear to possess an octahedric form. It is tolerably soluble in water, but insoluble in alcohol.

Thymine is distinguished from alanine by its want of taste.—*Ann. der Chem. und Pharm.*, lxxxix. p. 115.

On the Fluorides. *By* M. Fremy.

Some years since, M. Louyet communicated to the Academy several important facts relative to fluorine, hydrofluoric acid and the fluorides. According to M. Louyet, fluoride of mercury, heated

in tubes of fluoride of calcium, was decomposed by dry chlorine, furnishing fluorine; anhydrous hydrofluoric acid, prepared by a method of M. Louyet, did not act upon glass, and the equivalent of fluorine fixed by Berzelius must be replaced by a new number. The author having assisted in some experiments made by M. Louyet, and not being satisfied with them, has endeavoured to verify his facts.

Pure anhydrous hydrofluoric acid is prepared according to the author's method, by submitting hydrofluate of fluoride of potassium to distillation in a platinum retort. Thus obtained, it is gaseous at ordinary temperatures, but may be condensed by a freezing mixture of ice and salt; it then forms a very fluid liquid, which volatilizes as soon as it is taken out of the freezing mixture, acts upon water with the greatest energy, and diffuses in the air white fumes, which may be compared in intensity to those of fluoride of boron. Contrary to the assertion of M. Louyet, anhydrous hydrofluoric acid attacks glass with rapidity.

This acid may also be obtained by decomposing fluoride of lead by dry hydrogen; the action was carried on in a platinum tube, the fluoride being placed in a charcoal cup to avoid the action of the lead upon the platinum.

To avoid the errors of his predecessors caused by the employment of impure fluorides, the author has always made use of an acid prepared from crystallized and perfectly pure hydrofluate of fluoride of potassium. He has obtained some new fluorides and others presenting characters not given by Berzelius. The fluorides of zinc, iron, and lead were obtained in the crystalline form; protofluoride of tin was produced in very distinct and large prisms, and bifluoride of mercury in well-formed crystals. Fluoride of silver, which has been considered as uncrystallizable, deposits crystals of very regular form from its concentrated solution.

All the fluorides analysed by the author were obtained directly by the action of the pure acid upon the anhydrous or hydrated metallic oxides. Hydrofluoric acid does not act upon all the oxides which are attacked by muriatic acid; it would not combine with peroxide of gold or with peroxide of platinum. From this similarity in its action to an oxyacid, the author endeavoured to ascertain whether it really contained oxygen; but all his researches served only to confirm the views of its constitution generally admitted by chemists. From these researches it appears that fluorides are to be divided into three classes.

The first class includes the acid fluorides or hydrofluates of fluorides; these compounds are formed with great facility; they are decomposed by heat, furnishing when anhydrous, neutral fluorides and pure hydrofluoric acid; in many experiments they may replace hydrofluoric acid. By means of the potash salt, the author prepared the hydrofluoric æther of ordinary alcohol, by submitting to distillation a mixture of this salt with sulphovinate. This æther is gaseous, and resembles in its properties the corresponding compound of wood-spirit, discovered by MM. Dumas and Peligot.

The second class is composed of the hydrated neutral fluorides, characterized by the facility with which they are decomposed into hydrofluoric acid and oxides when we attempt to remove the water which enters into their composition; they appear to be true hydrofluates. Thus crystallized fluoride of silver, belonging to this class, evolves hydrofluoric acid, and produces oxide of silver when it is dried even *in vacuo*; when it is heated, it also evolves hydrofluoric acid and oxygen, and leaves a residue of very pure silver; it acts therefore as a hydrofluate of oxide of silver. Fluoride of mercury, when heated, acts in exactly the same manner.

The third class includes the anhydrous fluorides. These salts are not decomposable by heat, and may be decomposed, according to the metal they contain, by oxygen, hydrogen, chlorine, sulphuret of carbon and vapour of water.

The author attaches great importance to this classification of the fluorides, and thinks that it is from their having neglected it that his predecessors have fallen into such grave errors. Thus M. Louyet thought he isolated fluorine by decomposing fluoride of mercury by heat and chlorine; as fluoride of mercury belongs to the second or hydrated class, it behaves like a hydrofluate, and the gas obtained by M. Louyet was a simple mixture of hydrofluoric acid and oxygen. The author's analyses of fluorides for the determination of the equivalent of fluorine do not agree with those of M. Louyet, but confirm those of Berzelius.

With the view of obtaining fluorine, the author first turned his attention to the less oxidizable metals. But of these, the oxides gold and platinum do not combine with hydrofluoric acid; the fluoride of mercury is hydrated, and the fluoride of silver when anhydrous is undecomposable.

He therefore availed himself of a fact, ascertained in some experiments just made by him with Mr. E. Becquerel, from which it appeared that chloride of calcium in fusion is decomposed by the pile with great rapidity. By submitting the anhydrous fluorides of potassium, lead, and calcium to this process, the decomposition was readily effected, and a gas was liberated at the positive pole which quickly acted upon platinum. He was, however, unable to collect this gas, or to make any examination of it.

Sulphur, aided by heat, acts upon some anhydrous fluorides, displacing the fluorine; but compounds of fluorine and sulphur are then formed.

The action of dry chlorine on fluoride of calcium at a red heat decomposes the latter very slowly, disengaging a gas which attacks glass and platinum, and which appears to be fluorine. The experiments were carried on in platinum tubes, which are not acted upon by chlorine; and the latter gas was dried by being passed through several tubes containing anhydrous phosphoric acid, to avoid all chance of watery vapour.

Oxygen passing over fluoride of calcium at a red heat, decomposes it still more rapidly than chlorine, and also produces a gas which acts upon glass.—*Comptes Rendus*, Feb. 27, 1854, p. 393.

THE CHEMICAL GAZETTE.

No. CCLXXVI.—April 15, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Didymium and its Compounds. *By* M. MARIGNAC.

IN the separation of the oxides of lanthanium and didymium, the author adopted the process already described in his memoir on the atomic weight of these two metals*. He found it advantageous, however, to precede the separation of the sulphates by crystallization, by a very imperfect separation of the oxides, dissolving these in a considerable excess of nitric acid, and precipitating the solution by repeated additions of oxalic acid. The portions first precipitated are of a more distinct rose-red colour, and contain more didymium than the later portions; and the separation of the sulphates by crystallization takes place more rapidly when one oxide is present in much greater quantity than the other.

Atomic Weight of Didymium.—The author admits that in his former determinations the atomic weight of sulphate of didymium was stated too high. In these he endeavoured to ascertain how much chloride of barium was necessary for the decomposition of a known quantity of sulphate of didymium; but he now finds that even when an excess of chloride of barium is employed (this was afterwards separately determined in the filtrate from the precipitated sulphate of baryta), the sulphate of baryta when forming carries down with it sulphate of didymium, which cannot be got rid of by washing. The quantity of sulphate of didymium required for the precipitation of a known quantity of chloride of barium consequently appears too large by the weight of the salt thus carried down; and from this cause the atomic weight of sulphate of didymium was formerly calculated too high by the author. In fact, in his previous investigations*, the sum of the weights of sulphate of baryta, which were obtained in the decomposition of sulphate of didymium by a slight excess of chloride of barium, and then from the filtered liquid and wash-water, was somewhat larger than agreed with the weight of the chloride of barium employed for the precipitation: assuming that this excess represents the sulphate of didymium carried down with the precipitate, he now calculates from his former determinations the atomic weight of sulphate of didymium (O=100) at 1197·4, 1201·5, 1201·5, 1197·0, or on the average 1199·4.

* Chem. Gaz., vol. vii. p. 329.

By precipitating a weighed quantity of sulphate of didymium with oxalate of ammonia, washing the oxalate of didymium, which is insoluble in neutral fluids, and weighing the pure white oxide of didymium which remains after the calcination of the precipitate, 58·22, 58·24, 58·29, 58·31, 58·29 per cent. of oxide were found in the sulphate; the atomic weight of the oxide is therefore=696·8, 697·4, 698·7, 699·3, 698·6; on the average 698·2.

In experiments with the view of deducing the atomic weight of didymium from the composition of the chloride, the author found that chloride of didymium, even when dried in a stream of muriatic acid gas, or fused with chloride of ammonium, left a residue of oxychloride on being dissolved. He therefore removed the undissolved portion from the solution of chloride of didymium, and determined the chlorine as chloride of silver, and the oxide of didymium after precipitation with oxalate of ammonia. By comparison of the corresponding quantities of chloride of silver and oxide of didymium, he found the atomic weight of the latter to be=703·5, 698·9, 698·3, or on the average 700·2. From all these determinations he considers 700 to be the atomic weight of oxide of didymium, or a very close approximation to it, and 600 as that of didymium (O=100).

Didymium.—For the reduction of didymium, potassium was heated with chloride of didymium (which had been previously fused with chloride of ammonium) in a porcelain tube. Although it was pretty strongly heated, the resulting product was rather drossy than fused; when treated with water, chloride of potassium and chloride of didymium were dissolved, and a gray powder, which constantly evolved hydrogen gas, remained behind; this was a mixture of a gray metallic powder and a grayish-white crystalline powder (perhaps oxychloride of didymium); and these two constituents could not be separated by suspension in water. Brilliant sparks were produced when the powder was thrown into the flame of a spirit-lamp. In one instance the product of reduction contained two small metallic grains of a steel-gray colour, and with a tolerably bright lustre on their fractured surface, which however soon became dull; under the hammer they appeared slightly malleable before splitting. They did not fuse before the blowpipe, but were converted into oxide without any remarkable appearance of combustion; they did not appear to decompose water in the cold, but when left a long time in that fluid, were converted, perhaps by the influence of the atmospheric oxygen, into flocculent masses of oxide; in a diluted acid they produced a brisk evolution of hydrogen. The author adopts the opinion that only the pulverulent didymium decomposes water in the cold, but that the fused metal has no such effect.

Oxide of Didymium.—Didymium appears only to form one basic oxide, which may be prepared by heating to redness the nitrate, oxalate or carbonate, or the hydrate. After exposure to a strong red heat, it is pure white; a brown colour indicates the presence of superoxide. Hydrogen does not act upon it at a red heat. If it be once freed from superoxide, it remains perfectly white during exposure to a slight red heat in the air, or even during fusion with

nitrate of potash; but if it be heated after the addition of a little nitric acid, a dark brown colour again shows itself, and only disappears at a strong red heat.

Oxide of didymium is a strong base; even after strong calcination, it dissolves readily in dilute acids with considerable elevation of temperature; it dissolves by boiling in watery solutions of salts of ammonia, expelling the ammonia; it rapidly attracts carbonic acid from the air. In hot water it gradually becomes converted into hydrate. The hydrated oxide of didymium, precipitated by potash or ammonia from a solution of chloride of didymium, is gelatinous, and resembles precipitated alumina; it is of a very pale rose-red colour, and difficult to wash; during drying, it undergoes a considerable diminution of volume, and acquires a grayish rose-red colour. When dried *in vacuo*, and afterwards at 212° F., it still furnished 15 per cent. of water at a red heat, nearly agreeing with the formula DiO, HO (which requires 13·85 per cent. of water).

The salts of oxide of didymium are generally of a rose-red colour, frequently with a tinge of violet. Caustic alkalies and sulphuret of ammonium precipitate the gelatinous hydrate from its solution; alkaline carbonates and bicarbonates give protocarbonate of didymium, which is insoluble in an excess of the precipitant. The oxide of didymium is slowly, but completely precipitated from its salts by carbonate of baryta, even in the cold; oxalate of ammonia throws it down completely from a neutral solution; oxalic acid precipitates it almost entirely, if the solution does not contain a great excess of strong acid. Alkaline sulphates produce precipitates in solutions of oxide of didymium, instantaneously when the solutions are concentrated, after some time when they are diluted. These precipitates consist of double sulphates, of a pale rose colour, which are but sparingly soluble in water, and still more difficult of solution in an excess of the precipitant; the sulphate of didymium and soda is the least soluble. Phosphoric and arsenic acids produce precipitates by boiling; these are but little soluble in acids. Before the blowpipe, oxide of didymium gives a pale rose colour to borax and salt of phosphorus, like that produced by a very small quantity of oxide of manganese; it does not colour carbonate of soda.

Peroxide of Didymium.—This is produced by slightly calcining oxalate, carbonate, or nitrate of didymium; it is of a reddish-brown colour. It dissolves readily even in dilute acids, with evolution of oxygen; with muriatic acid it evolves chlorine; when boiled with it, it is very slowly converted into the hydrated oxide; it attracts carbonic acid from the air, and expels ammonia from its salts. It could not be obtained pure; the peroxide, prepared at different times, furnished on analysis (in which it was dissolved in a mixture of sulphurous acid, chloride of barium and muriatic acid, and the resulting sulphate of baryta determined) only 0·32–0·53 per cent. of oxygen, which was set free during solution in the acids.

Sulphuret of Didymium.—When oxide of didymium is heated to redness with carbonate of soda and sulphur, and the fused mass is extracted with water, there remains a grayish-white insoluble residue,

which after drying *in vacuo* loses nothing in weight when heated to redness in hydrogen gas. It dissolves entirely in dilute muriatic acid with a slight evolution of sulphuretted hydrogen; from analysis it appears to be an oxysulphuret, $Di^3 O^2 S$:—

	Calculated.	Found.	
Didymium	81·82	80·58	
Oxygen	9·09		
Sulphur	9·09	9·39	8·50

Sulphuret of didymium was prepared by passing over oxide of didymium at a red heat, a stream of vapour of sulphuret of carbon, conveyed by means of hydrogen gas. The sulphuret of didymium thus produced was pulverulent, and of a pale brownish-green colour; when moistened with water, it gave off an odour of sulphuretted hydrogen, without however evolving bubbles of this gas under water; it is decomposed, with evolution of sulphuretted hydrogen, even by very dilute acids; when heated upon platina foil, it is converted into a mixture of the oxide with the basic sulphate. 2·742 of oxide of didymium gave 3·124 of the sulphuret, so that the 0·392 of oxygen contained in the former were replaced by 0·774 of sulphur, whilst according to the formulæ DiO and DiS, 0·784 of sulphur ought to have been taken up.

Chloride of Didymium.—The solution of oxide of didymium in muriatic acid is of a pure rose colour; when sufficiently concentrated, it furnishes on cooling rose-coloured, deliquescent, rhombic prisms of hydrated chloride of didymium, which are often tolerably large. Their composition is DiCl+4HO:—

	Calculated.	Found.
Didymium	40·18	40·25
Chlorine	29·68	29·70
Water.....	30·14	31·78

These crystals are readily soluble in water and alcohol. A solution of chloride of didymium cannot be evaporated to dryness without evolution of muriatic acid gas and the formation of an oxychloride, which on solution in water remains as a white crystalline residue. When dried and fused in a current of muriatic gas, or mixed with chloride of ammonium and fused, chloride of didydium left some oxychloride on solution. For analysis the author employed fused chloride of didymium, and deducted the quantity of oxychloride contained in it; the results agreed with the formula DiCl:—

	Calculated.	Found.		
Didymium	57·52	57·48	57·61	57·59
Chlorine	42·48	42·25	42·62	42·63

The insoluble oxychloride, when dried *in vacuo*, loses no water at 212° F.; at a red heat it loses 10–11 per cent., but long calcination in the air drives off no chlorine, and it does not acquire a brown colour. Its composition did not appear to be constant, as indicated

by the following analyses; the calculation is made from the formula DiCl, 2DiO+3HO, and the water determined from the loss:—

	Calculated.	Found.		
Chloride of didymium ..	37·52	35·60	31·48	36·62
Oxide of didymium	50·35	53·36	55·64	52·09
Water	12·13	11·04	12·88	11·29

The author considers it possible that a portion of the oxide in these preparations may only be intermixed; when exposed to the air for a considerable time, they attracted carbonic acid.

Nitrate of Didymium is very readily soluble in water; the dilute solution is rose-red, but when more concentrated it is of a violet tinge. A syrupous solution solidifies on cooling into a deliquescent mass of crystals. The salt only becomes anhydrous at above 572° F., when it fuses; in this state it gave 50·48 per cent. of oxide of didymium, whilst calculation from the formula DiO, NO^5 gives 50·91 per cent. The anhydrous salt dissolves readily in alcohol of spec. grav. 0·811, and the solution is not rendered turbid even on the addition of much æther; nevertheless the salt does not dissolve in æther alone. If the salt, after fusion, be more strongly heated, abundant fumes of hyponitrous acid are evolved; the mass then becomes doughy, puffs up, and leaves behind a white porous mass, which is afterwards converted into brown peroxide. If the salt were only heated to the commencement of decomposition, it is resolved, on solution in water, into the neutral nitrate and a reddish-white insoluble residue, which contains nitric acid without nitrous acid, and of which the following analyses (made with two different preparations, dried at 212° F.) agree with the formula 4DiO, NO^5 +5HO. The author leaves it undecided whether the body in question may have been a mixture of a subnitrate with oxide or hydrated oxide:—

	Calculated.	Found.	
Oxide of didymium	69·35	68·75	71·20
Nitric acid.....	16·72	17·69	15·91
Water	13·93		

Phosphate of Didymium.—A concentrated solution of phosphoric acid furnishes a white pulverulent precipitate with a concentrated solution of nitrate of didymium only at the end of an hour or two. On the addition of a large quantity of water, this precipitate is immediately produced, and still more rapidly when the fluid is boiled. The greater part of the oxide of didymium is thrown down. The precipitate is insoluble in water, slightly soluble in dilute, but readily in concentrated strong acids. Dried *in vacuo*, it is 3DiO, PO^5 +2HO; it retains its water at 212° F., but loses it at a red heat:—

	Calculated.	Found.		Calculated.	Found.
3DiO ..	70·29	70·19	3DiO PO^5...	93·00	
PO^5	29·71	..	2HO	7·00	7·02

Arseniate of Didymium.—Arsenic acid does not precipitate solutions of salts of didymium in the cold even after standing a considerable time, but nearly all the oxide of didymium is thrown down by boiling in the form of a pulverulent precipitate. A precipitate of a similar composition is produced by neutral arseniate of potash in solutions of salts of didymium even in the cold; the compound thus thrown down is somewhat gelatinous, and after drying is still somewhat transparent and rose-coloured. Arseniate of didymium (prepared at different times), dried *in vacuo*, exhibited the anomalous composition $5DiO, 2AsO^5+2HO$; the water was only driven off at a red heat:—

	Calculated.	Found.				
Oxide of didymium..	53·03	52·94	53·34	54·04	53·98	53·50
AsO^5	43·56					
Water	3·41	4·32	3·86	3·88		

Carbonate of Didymium.—The voluminous rose-red precipitate produced by alkaline carbonates or bicarbonates in solutions of salts of didymium is insoluble in an excess of the precipitant; a precipitate thrown down by bicarbonate of ammonia from nitrate of didymium, when dried *in vacuo*, gave the composition DiO, CO^2+2HO; at 212° F. it still retained ½ an equivalent of water, but began to lose carbonic acid at this temperature:—

	Calculated.	Found.		Calculated.	Found.
DiO....	58·33	58·39	DiO....	67·88	68·46
CO^2 ..	22·92	22·95	CO^2....	26·66	25·63
2HO ..	18·75	..	½HO ..	5·46	

Sulphite of Didymium.—Strongly-calcined oxide of didymium suspended in water is readily dissolved by a stream of sulphurous acid; the solution is rose-red, and becomes turbid when heated from the separation of a light voluminous precipitate, which is again dissolved on cooling. If the excess of sulphurous acid be expelled by boiling, the precipitate becomes powdery and reddish-white, and no longer dissolves on cooling; the fluid then contains only traces of oxide of didymium. Dried *in vacuo*, this precipitate is DiO, SO^2+2HO:—

	Calculated.	Found.
Oxide of didymium	52·83	53·36
Sulphurous acid.....	30·19	30·42
Water.....	16·98	

Sulphate of Didymium.—The amount of water contained in the crystallized salt, which the author had previously described, turned out, upon more exact investigation, to be different, and to correspond with the unusual formula $3(DiO, SO^3)+8HO$, according to which we must calculate 20 per cent. of water; eight examinations of the crystallized salt gave 20·4–20·53, or on the average 20·20 per cent. of water; whilst the formula previously adopted by the author, DiO, SO^3+3HO, requires 21·95 per cent. When a solution of this

salt is heated, and especially when it is boiled, a crystalline precipitate is deposited, which has the composition $DiO, SO^3 + 2HO$ (found 14·76, calculated 15·79 per cent. of water). The solubility of the sulphate was different according as the anhydrous salt or one of the hydrates was employed; the following numbers give the quantities of the anhydrous salt contained in 100 parts of water under these different circumstances:—

	Employing		
At	DiO, SO^3.	$DiO, SO^3 + 2HO$.	$3(DiO, SO^3) + 8HO$.
53°·6 F.	43·1		
65°·4 F.	25·8	16·4	
66°·2 F.	..	..	11·7
78°·0 F.	20·6		
100°·4 F.	13·0		
104°·0 F.	..	..	8·8
122°·0 F.	11·0	..	6·5
212°·0 F.	..	..	1·7

Sulphate of didymium is not decomposed by a dull red heat, but at a bright red heat it loses two-thirds of the sulphuric acid contained in it; the residuary basic salt, $3DiO, SO^3$, is a white powder, insoluble both in cold and boiling water, and soluble very slowly in dilute muriatic acid even on boiling, but which dissolves readily in concentrated acids.

When solutions of the sulphates of didymium and ammonia are mixed, a pale red crystalline precipitate is deposited, sooner or later according to the concentration of the fluids; this requires about eighteen times its weight of water for its solution, but takes a still greater quantity of solution of sulphate of ammonia to produce the same effect. It consists of $3(DiO, SO^3) + NH^4 O, SO^3 + 8HO$:—

		Found.		
	Calculated.			
Sulphate of didymium ..	67·61	67·43	67·33	67·40
Sulphate of ammonia ..	15·49	15·87		
Water	16·90			

At 212° F. this double salt loses 6 equivs. of water (found 12·51 and 12·09 per cent.).

A reddish-white pulverulent precipitate is deposited almost immediately from a mixture of sulphate of didymium and sulphate of soda; this requires about 200 times its weight of water, and still more when sulphate of soda is present, for its solution. It furnished quantities of water varying between 5 and 10 per cent.; the calcined salt is $3(DiO, SO^3) + NaO, SO^3$:—

		Found.	
	Calculated.		
Oxide of didymium	46·78	45·78	45·75
Soda	8·67		
Sulphuric acid	44·55	45·78	45·13

When a concentrated solution of sulphate of potash is added to a similar solution of sulphate of didymium, and especially when the former salt is in excess, a white pulverulent precipitate is immediately produced, which gradually increases in quantity, acquires a granular and crystalline structure, and becomes more distinctly rose-coloured; it dissolves in about 63 times its weight of water. After boiling with water, the calcined precipitate consists of $3(DiO, SO^3) + KO, SO^3$ (found 44·96 and 44·9, calculated 44·79 per cent. of oxide of didymium; before boiling with water, the calcined salt contained only 39–42 per cent. of the oxide). The double salt, after long boiling with water, but without calcination, appeared to contain water in the proportion $3(DiO, SO^3) + KO, SO^3 + 2HO$ (found 4·93 and 4·66, calculated 4·57 per cent. of water).

Oxalate of Didymium.—This salt is precipitated from neutral fluids in the form of a pale reddish-white powder. It is dissolved by heat and the addition of nitric or muriatic acid, but separates on the cooling of the solution in a granular crystalline form, frequently even in rose-coloured crystals; these are rectangular prisms, terminated by pyramids, the surfaces of which are set on the angles of the prisms. The salt is insoluble in water, and nearly insoluble in oxalic acid and in strong mineral acids. The salt, dried in the air, slowly lost 20 per cent. of water at 212° F., and furnished 44–45 per cent. of oxide of didymium when heated to redness; the salt, dried at 212° F., gave 55·53 per cent. of oxide of didymium when calcined. The former is consequently $DiO, C^2O^3 + 4HO$, the latter $DiO, C^2O^3 + HO$:—

	Calculated.		Calculated.
DiO	43·75	DiO	55·45
C^2O^3 ..	28·12	C^2O^3 ..	35·64
4HO....	28·13	HO	8·91

The author always bore in mind the possibility that another metal might exist in the compounds examined by him, besides didymium. This possibility is however only supported by the circumstance that so small a quantity of oxide is converted into peroxide in the calcination of some of the salts, and by the unusual amount of water contained in the crystallized sulphate. All endeavours, either by fractional precipitation or decomposition, or by partial solution of the compounds to ascertain the admixture of any other metal, were however fruitless.—*Ann. de Chim. et de Phys.*, xxxviii. p. 148.

On the supposed new Metal Aridium. By M. Bahr.

Ullgren believed that the chrome-iron ore of Röras contained a new metal, for which he proposed the name of *Aridium**. The author has exactly repeated Ullgren's process for the preparation of the new metal, and has arrived at the conclusion, that the so-called aridium consists of iron, containing phosphorus and probably some chromium.—*Journ. für Prakt. Chem.*, lx. p. 27.

* Chem. Gaz., vol. viii. p. 289.

On Niobic, Pelopic and Tantalic Acids. By H. Rose.

The author has already pointed out the differences which these three acids exhibit in their behaviour *. From his observations it appeared that pelopic acid exhibits a great resemblance to tantalic acid, and that both acids differ far more widely from niobic acid.

Further experiments have proved that tantalic acid is decidedly distinct from pelopic acid. But between this latter acid and niobic acid, which were found together in the columbites of Bavaria and North America, a remarkable and unexpected connexion has been discovered.

These two acids were formerly prepared, by means of water, from the chlorides, corresponding with them in composition, as other modes of operation did not appear so advantageous. The separation of the two acids however was always imperfect, and even when it was often repeated, by decomposing the chlorides by means of water into the corresponding acids, and converting these again into chlorides by treatment with charcoal and chlorine, they could not be obtained in a tolerably pure state, although the conversion of the acids into chloride was repeated perhaps twenty to thirty times.

After many careful experiments had been made in vain, a small quantity of niobic acid, prepared from pure niobate of soda, was converted, under peculiar circumstances, into chloride. It was mixed with an extremely large quantity of charcoal, and exposed to a very strong stream of chlorine gas, and at first with a very gentle heat. This experiment led to the most surprising results. The pure niobic acid furnished the purest yellow chloride of pelopium, instead of the white chloride of niobium; and this result could always be obtained afterwards, but only by observing a number of precautions, which the author fully describes. By following a modified process, on the contrary, the white chloride could be prepared from the same acid.

It appears from the production of these two chlorides, that the same metal is contained in them, as well as in the acids prepared from them by means of water. But either of these acids, when once formed, like the corresponding chloride, can only be converted into the other by indirect methods.

The amount of oxygen contained in the two acids has not yet been directly ascertained; but as the yellow chloride (chloride of pelopium) contains more chlorine than the white chloride (chloride of niobium), it follows that pelopic acid must contain more oxygen than niobic acid. But the latter cannot be converted into pelopic acid in any way, even by the most powerful oxidizing agents. This can be effected neither by direct nor by indirect oxidation. Moreover, the behaviour of the two acids before the blowpipe is different. It appears however that some oxygen may be extracted from the acid representing the yellow chloride by a few reducing agents.

* Chem. Gaz., vol. iii. p. 35, and vol. iv. p. 349.

The proportion of oxygen in the two acids, calculated from the amount of chlorine in the chlorides, is very anomalous, a similar proportion occurring only in two of the oxides of sulphur.

It is still doubtful whether the white chloride, even when prepared with care, does not still contain a small quantity of oxygen; so that it may be regarded as an aci-chloride. If present, however, it appears from the most careful experiments to be extremely small; so that we may still hope to obtain the chloride perfectly free from oxygen.

As, however, in any case, pelopic and niobic acids are oxides of the same metal, the latter must receive only a single name. The author decides in favour of the name niobium. The highest state of oxidation of this metal must therefore be called niobic acid; this is the acid which is produced from the yellow chloride, with which it corresponds in composition; it is the acid hitherto called pelopic acid. — *Bericht der Akad. der Wiss. zu Berlin*, 1853, p. 604.

On Pyrotartrate of Ammonia. *By* A. E. Arppe.

If dry ammonia be passed into a solution of pyrotartaric acid in alcohol of spec. grav. 0·80, bipyrotartrate of ammonia first separates; if the introduction of the ammonia be continued, this is converted into the neutral salt.

Neutral Pyrotartrate of Ammonia is a white crystalline powder, which under the microscope appears to consist of prismatic crystals. It is readily soluble in water, but difficult of solution in alcohol; when boiled in alcohol, it is converted into the acid salt. With potash it evolves ammonia. When heated, it has an odour of ammonia; at 194°–212° F., this is evolved plentifully, whilst the acid salt is formed. The latter may be heated nearly to 284° F. without decomposition.

If the neutral or acid salt be distilled, an ammoniacal distillate is obtained, together with a crystallizable substance, to which the author gives the name of *bipyrotartramide*, or by abbreviation *bipyrtramide*.

Bipyrotartramide is $C^{10} H^7 NO^4$; it is produced from the pipyrotartrate of ammonia, $NH^4 O, 2C^5 H^3 O^3 + HO$, by the loss of 4HO. It is most readily obtained when the distillation is carried on at the lowest possible temperature. When pure, it is colourless and inodorous, and has a cooling, slightly bitter and acid taste; dissolved in water, it acts upon litmus-paper like an acid, but has otherwise none of the properties of a true acid. Thus it does not combine with ammonia; and if it expels carbonic acid from carbonate of ammonia, this arises from impurity. It fuses at 151° F., when it runs like an oil, and leaves a permanent fatty mark upon paper. On cooling, it sets into a crystalline mass, which is fatty to the touch, and has a laminar fracture. The crystallization proceeds from a central point; and in this manner, very regular, circular,

radiate discs are formed, especially when the quantities are small. It evaporates even on the water-bath, but does not boil until it reaches 536° F.; it does not however possess a constant boiling-point; at about 572° F. it is driven off rapidly, leaving a carbonaceous residue. By distillation it is generally obtained as a thick crystalline mass; if the heat be carefully applied, it sublimes partially in thin shining laminæ, not unlike naphthaline, or becomes deposited in distinctly-formed crystals.

It crystallizes from its solutions in æther, alcohol and water, in fine shining needles. Impure bipyrotartramide may remain fluid for a considerable time at ordinary temperatures if it contains a trace of water. It dissolves in water, æther, alcohol, the ordinary acids and alkalies; it is anhydrous. Its crystals belong to the rhombic system. It is decomposed by boiling with a great excess of a concentrated solution of potash; an abundant evolution of ammoniacal vapours takes place, and the salt is converted into bipyrotartrate of potash, which, after the alkaline solution has been saturated with acetic acid, crystallizes almost instantaneously in its readily recognizable form. Analysis:—

Carbon	52·96	52·91	10 =	60	53·10
Hydrogen	6·17	6·17	7	7	6·19
Nitrogen	..	12·60	1	14	12·39
Oxygen	28·27	28·32	4	32	28·32

Bipyrotartramide corresponds to bisuccinamide. It dissolves oxide of lead in abundance. When this solution is filtered, even if it be considerably diluted, the paper is attacked by it in a remarkable manner; it swells up, becomes slimy or gelatinous, and dries into a hard corneous substance, which when ignited smoulders away like tinder, whilst metallic lead is reduced. When evaporated in a dry atmosphere, it is converted, although very slowly, into a shining, brittle, gum-like mass, which dissolves in water with a milky appearance, and is decomposed by alkalies, with deposition of hydrated oxide of lead. This lead compound has the following composition:—

Bipyrotartramide	27·30	2 =	226·0	27·24
Oxide of lead	67·23	5	558·5	67·33
Water	5·47	5	45·0	5·43

Bipyrotartramide does not combine with oxide of silver.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 228.

On Carolathine. *By* F. L. Sonnenschein.

The author has examined a new mineral, resembling mellite, which was sent to the Royal Museum at Berlin by Prince von Schönaich-Carolath. It consists of alumina, silica, water, and a sub-

stance containing carbon, the nature of which however has not yet been exactly ascertained.

Carolathine, as the author calls this mineral, occurs either in separate fragments, or coating the surfaces of clefts; partly solid, with a shelly fracture; partly aggregated together in balls; it is sometimes earthy and pulverulent, of a honey- or dark wine-yellow colour, transparent at the edges, and with a slight fatty lustre. It is very brittle, harder than gypsum, but not so hard as calc-spar, although nearly equalling it. Crystals have not been observed. Its specific gravity, according to a preliminary determination, is 1·515.

Heated in a glass retort, it gives off considerable quantities of water, sometimes accompanied by decrepitation; at an elevated temperature the residue acquires a darker colour, and leaves a black, shining, brittle mass, which does not cake together even with the strongest blast-furnace. The condensed water has a neutral reaction; and when the substance is perfectly free from intermixture of carbonaceous particles, it is quite inodorous and colourless, and without any empyreumatic impurities.

Before the blowpipe it smoulders away without flame, and exhibits reactions of alumina and silica. It is soluble in caustic soda, and is decomposed by muriatic acid, forming a yellowish solution, whilst silica is separated. The solution contains, besides alumina and a carbonaceous compound which causes the coloration, small quantities of oxide of iron; it contained no other constituents, with the exception of traces of phosphoric acid, which were indicated by molybdate of ammonia. Analysis gave:—

		The combustible substance.	
Al^2O^3	47·25	Carbon	2·41
SiO^3	29·62	Hydrogen	1·33
Combustible	23·13	Oxygen	19·39

When heated to 554° F., the mineral lost 15·10 per cent. of water, but still retained some; it could not therefore be ascertained how much of the hydrogen of the combustible substance was proper to it. The silicate of alumina agrees with the formula $(Al^2O^3)^3 + (SiO^3)^2$.—*Journ. für Prakt. Chem.*, lx. p. 267.

On the Preparation of Uric Acid. *By* E. Arppe.

10 oz. of borax are boiled with 70 lbs. of water in a pot, in which two bags, each containing 3½ lbs. of dried pigeon's dung, are hung. ½ a pound of muriate of ammonia is then added, and the whole allowed to stand for twelve hours. The precipitate is washed by decantation, dissolved again in a dilute solution of borax, which leaves behind a considerable quantity of a slimy matter; it is then separated by the addition of sulphuric acid, and purified by treating

it with potash, and decomposing the potash salt with sulphuric acid. —*Ann. der Chem. und Pharm.*, lxxxvii. p. 237.

On Muriate of Roseo-cobaltia and Luteo-cobaltia. *By* Prof. W. Gregory.

The red and yellow salts first discovered by Genth, and afterwards observed by Claudet and Fremy*, for which the latter chemist proposed the above names, have been analysed by Gregory. Fremy's formula for the red salt, $Co^2 Cl^3$, $5NH^3$, HO, is incorrect; the salt contains no oxygen or water. The author finds Claudet's formula, $Co^2 Cl^3$, $5NH^3$, perfectly correct. He also confirms Fremy's formula for the yellow salt, $Co^2 Cl^3$, $6NH^3$.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 125.

Oxidized Silver.

The high appreciation in which ornaments in oxidized silver are now held, render a notice of the process followed interesting. There are two distinct shades in use, one produced by chlorine, which has a brownish tint, and the other by sulphur, which has a bluish-black tint. To produce the former, it is only necessary to wash the article with a solution of sal-ammoniac; a much more beautiful tint may however be obtained, by employing a solution composed of equal parts of sulphate of copper and sal-ammoniac in vinegar. The fine black tint may be produced by a slightly warm solution of sulphuret of potassium or sodium.—*Journal of Industrial Progress*, April 1854.

ANALYTICAL CHEMISTRY.

On the Employment of Molybdate of Ammonia for the Detection of Arsenic. *By* H. Struve.

Some time ago, the author, in conjunction with Prof. Svanberg, suggested the use of molybdate of ammonia for the detection of phosphoric acid; subsequently H. Rose showed that it formed a similar compound with arsenic acid.

The author now proposes to make use of this property of molybdate of ammonia, to show in medico-legal analyses that the spot obtained by Marsh's apparatus is produced by arsenic; and when arsenic is present in any substance, to separate it in such a compound as may be afterwards tested in Marsh's apparatus.

The phænomena of this reaction depend upon the peculiar behaviour of a solution of arsenic acid towards a great excess of a solution of molybdate of ammonia in nitric acid under the influence of heat. In this case, as with phosphoric acid, a yellow precipitate, in

* Chem. Gaz., vol. xi. p. 201.

well-formed but microscopic dodecahedra, is separated; this precipitate is insoluble in acids and in many saline solutions. Concentrated sulphuric acid at ordinary temperatures has no action upon this compound; but when heated, dissolves it completely, forming a colourless solution, from which no precipitate is produced on dilution with water. The precipitate consists of pentamolybdate of ammonia, in which about 7 per cent. of arsenic is present.

If this salt, after drying, be heated in a thin glass tube closed at the bottom, it is decomposed with evolution of water and ammonia, whilst arsenious acid sublimes and oxide of molybdenum remains behind. If the compound has been previously mixed with a little charcoal, metallic arsenic is sublimed, by which means the presence of arsenic in this substance may be readily shown.

If the yellow salt be put with zinc, sulphuric acid, and water into a gas-bottle, arseniuretted hydrogen gas is not evolved until after some time, partly because the insolubility of the compound in dilute acids causes it to elude the action of the zinc, and partly because the molybdic acid must first be reduced to oxide. In one experiment, traces of arseniuretted hydrogen gas only made their appearance a quarter of an hour after the addition of the yellow compound; up to that time nothing but pure hydrogen was evolved.

To cause the instantaneous formation and evolution of arseniuretted hydrogen gas with this compound, all that is necessary is to break up the combination of the arsenio-molybdate of ammonia. This may be effected by any alkali (ammonia is the best), or by boiling with concentrated sulphuric acid.

The mode of employing this test for arsenic is as follows:—Suppose that by means of Marsh's apparatus the well-known spot has been produced in a glass tube or on a porcelain slab, and that it is desired to determine whether it does or does not arise from arsenic.

For this purpose the spot is to be dissolved by heat in a small quantity of concentrated nitric acid; the solution is put with a few drops of water into a test-glass; a great excess of the solution of molybdate of ammonia in nitric acid is then added, and the whole heated to boiling. If the spot were produced by arsenic, a yellow precipitate is formed, either immediately, or, if the spot to be tested were very small, after standing some time; this is a most unequivocal indication of the presence of arsenic. The appearance of the reaction is considerably hastened when the test-tube with its contents is exposed for some time to the heat of the sand-bath, as in this case the same effect is produced by the continued action of heat, as in other cases is done by time. This method of ascertaining the presence of arsenic after its oxidation into arsenic acid is so sensitive, that a perfectly distinct precipitate may be obtained after a little time from solutions which do not contain more than 1-30,000dth of arsenic acid. The reaction is no longer produced in solutions containing only 1-60,000dth of arsenic acid.

When other metals are to be tested for arsenic, in which the re-

action with the blowpipe cannot be employed, the molybdate of ammonia may be used with advantage. This is especially the case when antimony or tin are to be tested for arsenical impurities. In these cases all that is necessary is to oxidize a small quantity of the metal to be examined by concentrated nitric acid, to collect the oxide formed upon a filter, and test the filtrate. The presence of other metals does not prevent the reaction, as they are all soluble in nitric acid.

The above behaviour of arsenic acid is also employed by the author for the separation of the arsenic from any compound, in such a form that it may be treated in Marsh's apparatus without the necessity of a subsequent examination of the arsenical spots. The operations required for this purpose are the following:—

The substance to be tested for arsenic is treated in a glass flask with chlorate of potash and muriatic acid, until the greater portion of the organic substances is destroyed, and the solution has acquired a pale brown colour. The contents of the flask are then evaporated to dryness in a porcelain cup, in order to expel the excess of acid; it is then dissolved in water and filtered. The clear solution is evaporated to a small volume, and after cooling, a solution of molybdate of ammonia in nitric acid is added to it in excess, when a yellow precipitate is instantaneously thrown down. If nothing further is separated on the addition of more of the precipitant, the precipitate is collected on a filter, washed with water containing nitric acid, and characterized by the letter A. The filtrate is placed with the wash-water upon the sand-bath until the solution is brought to a boiling heat, at which it is kept for some time. The action of heat causes the separation of a fresh precipitate, which is collected when it no longer appears to increase, and characterized by the letter B.

The precipitate A, separated at the usual temperature, consists of phospho-molybdate of ammonia; and if all heating of the solution has been avoided during the addition of the precipitant, it contains no trace of arsenio-molybdate of ammonia. The phosphoric acid required for the formation of this precipitate is derived from the organic matter, in which phosphorus is present, partly as phosphoric acid, and partly in proteine compounds containing phosphorus. If it be not certain that all heating of the fluid was avoided during the addition of the precipitant, it is possible that small portions of arsenic acid may be in this precipitate A, and in that case a testing of this salt by Marsh's apparatus is always necessary.

The precipitate B, which is produced by heat, consists partly of small portions of phospho-molybdate of ammonia, as this compound does not separate completely until the solution is gently heated; but if arsenic be present in the substance under examination, principally of arsenio-molybdate of ammonia. A portion of this precipitate is consequently tested in Marsh's apparatus after it has been dissolved in ammonia. If the substance contained arsenic, it is certain to be found in the precipitate B, and may be recognized by the spot

furnished by Marsh's apparatus, which can then be due to nothing else. — *Bull. de St. Pétersb.*; *Journ. für Prakt. Chem.*, lviii. p. 493.

On the Determination of Iodine. *By* R. Kersting.

The author has instituted some experiments upon the estimation of iodine, especially with a view to finding a method for the more exact determination of this substance in the urine. Having found that the cyanide of potassium, formed by incineration with potash, prevented the precipitation by chloride of palladium, as both free hydrocyanic acid and cyanides dissolve iodide of palladium, he distilled the urine with sulphuric acid. Solutions of iodine, as well as urine containing iodine, when they have been distilled to the concentration of the sulphuric acid, part with their iodine. According to the author, determinations of iodine may be completed within two hours by the following process:—

If the fluids be very poor in iodine, potash is to be added to them; 200–250 cub. centims. are then to be distilled down to 20–40 cub. centims.; the distillate is free of iodine. The residue is mixed without shaking with 20 cub. centims. of sulphuric acid. The distillate contains iodine, hydriodic acid, sulphurous acid, sulphuric acid, carbonic acid, and the volatile acids of the contents of the retort.

It is necessary to convert the sulphurous acid into sulphuric acid. For this purpose three fluids are to be prepared, viz. 1st, a saturated solution of chloride of lime; 2nd, the solution of sulphurous acid or bisulphite of soda; 3rd, a solution of 1 part of starch in $\frac{1}{10}$th of sulphuric acid and 24 parts of water. 1 or 2 drops of the solution of starch are first added to the fluid; this is followed by the solution of chloride of lime, which is added until the production of a blue colour; the solution of sulphurous acid is then added until this colour just disappears. In this manner the fluid is rendered fit for determination by means of chloride of palladium.

In determinations of iodine it is necessary to concentrate the fluids. If they be too much diluted, all the iodine does not pass over. In this remark the author wishes to correct a statement of Osann, according to whom, when dilute fluids are distilled with sulphuric acid, all the iodine is obtained; and to prove its correctness, he has instituted special experiments. These show that dilution does not prevent the formation of hydriodic acid, which, as it is not readily volatilized, remains in part in the retort. Nor does the addition of oxidizing substances, such as nitrosulphuric acid, chlorate of potash, or hypochlorite of lime with muriatic acid, and solution of chlorine or bromine give the whole of the iodine. When from one-half to one-eighth of the fluid has distilled over, the fluid in the retort still contains iodic acid.

Direct precipitation of the iodine by protochloride of palladium

may also, under some circumstances, take place very imperfectly. The addition of protochloride of palladium to urine containing iodine produces a precipitate, which contains protiodide of palladium, an organic salt of palladium and reduced metal. 1 part of the protiodide of palladium always remains dissolved in the urine. This solution, when starch and solution of chlorine or bromine are added to it, gives no reaction of iodine; if it be evaporated to dryness with potash and ignited, then dissolved in water and the solution tested, iodine, which was not precipitated by the protochloride of palladium, will always be detected. Protiodide of copper behaves in the same manner.

The extraction of the iodine by chloroform, according to Rabourdin's method, is so far valuable that the chloroform always takes up some iodine, with which it settles to the bottom of watery fluids; but it cannot be recommended for quantitative determinations, as the quantities which it extracts from a fluid are very unequal.

Volumetric Determination of Iodine by Protochloride of Palladium.—If an excess of chloride of palladium and muriatic acid be added to a solution of a metallic iodide, and the whole heated to 140°–212° F., and shaken, the iodide of palladium separates in black flakes, which are of a caseous consistence, like chloride of silver. But if iodine be present in excess, the precipitate is only deposited with difficulty. A millionth of iodine in a solution will still be indicated by the fluid acquiring a brown colour. Iodine may consequently be determined volumetrically by means of protochloride of palladium. For this purpose three fluids are employed:—

1. *Pure Solution of Iodide of Potassium*, containing exactly $\frac{1}{1000}$dth of iodine.

2. *Acid Solution of Protochloride of Palladium*, containing $\frac{1}{2370}$dth of palladium. This is prepared from the metal, by dissolving 1 part of it by heat in nitromuriatic acid, evaporating the salt to dryness at 212° F., adding to this 50 parts of concentrated muriatic acid and 2000 parts of water, and leaving the solution to become clear by standing. The exact determination of the strength is effected by the solution of iodide of potassium.

3. *The Solution of Iodine to be tested.*—If the iodine compound be dry and in a suitable form, it is to be dissolved in a small quantity of water; an approximate determination of the amount of iodine is then made by the method described below; the remainder of the solution is diluted to contain about $\frac{1}{1000}$dth of iodine, and then again determined exactly. When urine containing iodine is to be analysed, the acid distillate, obtained as above directed, is employed.

These fluids are employed in the following manner:—10 cub. centims. of the solution of protochloride of palladium are poured into a white bottle capable of containing 100–200 cub. centims.; the bottle is then lightly corked, and placed in a pot with hot water (140°–212° F.). The solution of iodine is now added from a burette, and the whole is shaken and heated for some seconds. As

soon as the fluid is clear, some of it is to be poured into two colourless test-glasses, so as to fill about 2 inches of both. If a few drops of solution of iodine be added now to one glass, it may be seen by comparison with the other whether any brown tinge is produced. The necessary quantity of iodine, as nearly as can be judged, is then added, the contents of the test-glasses are returned into the first vessel, which is heated, shaken, left standing, and again tested in the test-glass; this is continued until a fresh addition of iodine no longer produces any coloration. Lastly, a filtered sample is to be tested; and if neither the addition of solution of iodine nor of solution of palladium produce any brown colour in this, it can scarcely contain an excess of a millionth part of either of these substances. No perceptible error occurred in testing the distillate of urine, although this fluid of itself communicates a slight colour to solution of palladium. Such a determination as this may be effected with properly-prepared solution of iodine in 10–15 minutes. If it be required to determine the palladium for the more exact dilution of the crude solution No. 2, 10 cub. centims. of this are precipitated with the solution of iodine No. 1. Each cubic centimetre of the latter represents 0·42 milligrm. of palladium. The amount of iodine in the solution No. 3 is determined with the standard solution of palladium No. 2, each cubic centimetre of which represents 1 milligrm. of iodine.

The author then ascertained, by a series of experiments, what bodies had no effect upon the reaction on which this method of volumetric analysis depends. These are,—dilute muriatic acid, sulphuric acid, phosphoric acid, nitric acid and acetic acid; as also the neutral potash, soda, and ammoniacal salts of these acids; chloride of calcium, chloride of zinc, acetate of lead, sugar, uric acid, the distillate of urine with sulphuric acid, alcohol, æther, oil of lemons, starch-paste and bromide of sodium; the latter however only when no free mineral acid is present at the same time; the presence of acetic acid is not disadvantageous. The following, on the contrary, have a preventive action:—Free alkalies, which precipitate protoxide of palladium; free chlorine, bromine and iodine, cyanogen, much nitric acid when heated, and sulphurous acid. The preventive agents can generally be got rid of. The alkalies are saturated with sulphuric acid. Free chlorine, bromine, and iodine are converted by watery sulphurous acid, in the presence of 1 or 2 drops of starch-paste, into hydracids, and these neutralized by potash. Sulphurous acid is oxidized by solution of chloride of lime and muriatic acid, so as to form sulphuric acid. In this operation starch-paste indicates the exact point of saturation; the commencement of blue coloration shows an excess of chlorine; its disappearance on the addition of sulphurous acid indicates the saturation of the chlorine.

Volumetric Determination of Iodine by Bichloride of Mercury.—Blue iodide of starch is discoloured by bichloride of mercury, with formation of iodide of mercury and chlorine. If we use a mixture

of blue iodide of starch and hydriodates, the salts are first decomposed, and then the iodide of starch. A solution, so diluted as to contain only 1-10,000dth of iodine, retains the iodide of mercury formed in solution, so that the discoloration of the iodide of starch is produced very distinctly. For these determinations the following fluids are prepared:—

1. Pure solution of iodide of potassium, containing 1-10,000dth of iodine. 1·308 grm. of calcined iodide of potassium are dissolved in water to form 100 cub. centims. of fluid. 10 cub. centims. of this, mixed with water sufficient to form 1000 cub. centims., give a solution containing 1-10,000dth of iodine.

2. *Solution of Bromine.*—Water shaken up with an excess of bromine contains about $\frac{1}{32}$ bromine; this, when diluted with 49 vols. of water, gives a solution of $\frac{1}{1600}$dth of bromine.

3. *Starch-paste*, prepared by boiling 1 part of starch with $\frac{1}{10}$th of sulphuric acid and 24 parts. of water.

4. *Solution of Bichloride of Mercury* with $\frac{1}{1000}$dth HgCl.—1 grm. of the salt is dissolved in 1000 grms. of water by heat. It is valued by means of the iodide of potassium solution No. 1.

The fluid containing an iodine compound to which this method is applicable must be so far diluted as to contain about 1-10,000dth of iodine, and then tested exactly for this substance. With this view the quantity of solution of bichloride of mercury required to saturate 1 part by weight of iodine is first ascertained. 100 cub. centims. of the solution of iodine No. 1 (containing 0·010 grm. of iodine), are poured into a white beaker capable of holding 1–2 litres, and 10 drops of starch-paste and 10 drops of solution of bromine are added to them. The fluid appears deep blue. The solution of bichloride of mercury is now poured in from the burette, the solution of iodine being kept constantly shaken until the blue colour has completely disappeared. The number of cubic centimetres employed represents a quantity of 0·010 grm. of iodine, and is marked upon the vessel in which the mercurial solution is kept. According to the experiments, 10 cub. centims. of this solution were required, and therefore 1·1 cub. centim. to 1 milligrm. of iodine. When the unknown solution of iodine, No. 5, is treated in the same manner, the volume of the standard mercurial solution gives the amount of iodine.

The reaction upon which this method depends is not prevented by the presence of neutral sulphate, phosphate, or nitrate of soda, sulphate of ammonia, acetate of lead, concentrated acetic acid or sugar. On the other hand, the following have a preventive action: —Free mineral acids, and also acetic acid and its salts when the quantity of the latter is about 20 times that of the iodine. The most important thing is, that muriatic and hydrobromic acids are also preventives. All these substances necessitate the employment of a larger quantity of solution of bichloride of mercury for the complete decolorization of the iodide of starch. Free alkalies, on the contrary, strongly deoxidizing bodies (such as sulphurous acid),

and various organic compounds (even urine), also destroy the action, because they decolorize the iodide of starch directly.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 19.

PATENT.

Patent granted to F. M. Lyte, *for Improvements in obtaining Iodide of Potassium, when treating certain Metals.*

This invention consists in the discovery, that when the chlorides, or some soluble salts of certain metals, are placed in contact with solutions containing mixed iodides and chlorides, double decomposition ensues, and insoluble metallic iodides are formed, and that, by continuing the addition of the chlorides, this continues so long as any soluble iodide remains in the solution; also that the insoluble iodide can afterwards be converted into a metal and a soluble iodide by any of the processes in use at present for the decomposition of metallic chlorides, as in refining silver. For instance, the patentee refines silver, and at the same time produces iodide of potassium from such solutions as bittern, or matters which contain these mixed iodides and chlorides. Having dissolved the silver in nitric acid, and precipitated it with a soluble chloride, as chloride of silver, he divests it of copper by washing with water. He then projects the chloride so produced into the solution of mixed chlorides and iodides, and continues the addition, with frequent stirring, till, on adding a portion of the chloride of silver to a test-sample of the liquid, it ceases to become yellow. Then, to ensure all the silver being converted into iodide, he adds a very small portion more of the mixed salts, so that there may be a small excess of iodine in the solution, rather than a trace of chlorine in the precipitate. The addition of ammonia facilitates the decomposition; so also does heating the liquid. The iodide of silver thus produced is converted into iodide of potassium and metallic silver by projecting it, when completely desiccated, into a crucible containing fused carbonate of potash, according to the method now in use for the reduction of the chloride; but by this process iodide of potassium is formed, instead of the chloride as formerly,—a valuable product, instead of a product of little value.

By adding a soluble salt of lead to the mixed salts till all the iodine is precipitated, and decomposing the iodide thus formed by the same method, iodide of potassium is formed, which may be dissolved and purified by recrystallization.

The periodide of mercury (a most splendid pigment) is produced by adding the bichloride of mercury to the mixed salts.

By these methods all the iodine is recoverable from the mixed salts; whereas by the old process generally used, a great deal was lost as chloride of iodine.—Sealed July 26, 1853.

THE CHEMICAL GAZETTE.

No. CCLXXVII.—May 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Investigation of the Constituents of the Seeds of Peganum Harmala. *By* J. Fritzsche.

The author has already shown (Chem. Gaz., vol. vi. p. 398) how nitroharmalidine is obtained from harmaline. He now states that it may be procured without the assistance of alcohol.

2 parts of water are poured over 1 part of harmaline; to this mixture a sufficient quantity of acetic acid for the solution of the harmaline is added, and the solution thus obtained allowed to flow in a slender stream into 24 parts of boiling nitric acid of spec. grav. 1·120. When the mixture is completed, and the violent evolution of red fumes which accompanies it has become somewhat less, the lamp is removed, and the fluid, which still effervesces strongly, is allowed to cool as rapidly as possible in order to check the further action of the nitric acid; an excess of alkali is added to the cold fluid, by which the nitroharmalidine is precipitated, whilst the principal collateral product, a resin, remains dissolved. The precipitate is collected upon a filter, dissolved after sufficient washing in dilute acetic acid, triturating the resinous masses which usually occur in it, and the nitroharmalidine then precipitated from the solution by chloride of sodium in the form of the muriate. This is collected upon a filter, washed with a saturated solution of chloride of sodium, and dissolved from the filter by pouring lukewarm water over it; from this solution the alkaloid is precipitated by alkali. In this manner the author repeatedly obtained, without any failure, nitroharmalidine free from other alkaloids.

Other products are obtained when the nitric acid has been permitted to act too long upon the harmaline, or when a concentrated acid has been employed. A new alkaloid is then formed, which may also be obtained directly from nitroharmalidine by the action of nitric acid, and which therefore is properly to be regarded as a product of the transformation of nitroharmalidine; this is

Nitroharmidine, $C^{26}H^{22}N^{6}O^{6}$.—2 parts of water are poured over 1 part of harmaline; to the mixture a sufficient quantity of acetic acid is added to dissolve the harmaline, and the solution is allowed to flow slowly in a small stream into 12 parts of boiling nitric acid

of spec. grav. 1·40. When the addition, during which a violent evolution of red fumes is produced, is completed, the fluid is still kept boiling for a short time, when it is found to contain neither harmaline nor nitroharmalidine, but principally nitroharmidine. If the fluid, which has an orange-yellow colour, be now allowed to cool slowly, the separation of a crystalline product, consisting principally of nitrate of nitroharmidine, soon commences, and continues for a considerable time, especially if the acid be allowed to evaporate gradually at the ordinary temperature. It may be obtained tolerably pure by collecting it on a filter and washing it with alcohol; but a considerable quantity of the alkaloid always remains dissolved in the mother-liquor. The best plan is to cool the fluid immediately after the completion of the action, either by putting snow or ice into it, or by placing it in cold water, and then adding to it an excess of caustic alkali. By mixing the acid fluid with water, or by the melting of ice in it, it is rendered milky at first, owing to the separation of the resinous body, which always occurs as a subordinate product; it however gradually becomes clear again, the resin collecting into small masses. The same thing takes place when an alkaline solution is added to the clear fluid, which has been cooled without addition of water, and the same resinous body is also separated, even during the action of nitric acid upon harmaline, if a smaller quantity of the acid than above mentioned be employed, or if the acid be gradually added to the harmaline. This resinous compound is soluble in alkalies, so that when a sufficient excess of alkali is used for the precipitation of the alkaloid, a deep reddish-brown alkaline solution of the resin is obtained, together with a deep yellow precipitate of the alkaloid, which is usually mixed with only a few little masses of resin, covered externally with the alkaloid. The greatest part of this precipitate consists of nitroharmidine; nevertheless if the nitric acid contained chlorine, it contains more or less of another new alkaloid. To prepare pure nitroharmidine from it, the following process must be adopted:—Hot water is poured over the precipitate, and muriatic acid added to the mixture in drops until complete solution of the alkaloid is effected; this solution is filtered whilst hot, and left to cool; concentrated muriatic acid is then added to it until a turbidity, caused by the deposition of microscopic crystals, is produced in it. The fluid is now left at rest for some time, when the greater part of the nitroharmidine separates as muriate in acicular crystals, whilst any small quantity of the other alkaloid remains dissolved; the whole is then filtered, and the crystals washed with a little dilute muriatic acid. To separate the alkaloid from them, they are dissolved in boiling water, and ammonia is dropped into the boiling solution, which is kept constantly stirred; by this means the nitroharmidine is immediately separated in yellow flakes, exactly as in cold solutions; but whilst in the latter the flakes long retain a gelatinous appearance, and can consequently only be very slowly washed, in boiling fluids they are very soon converted into fine needles, which may be very easily washed. The product thus obtained is dried, and dissolved in strong alcohol with the aid of heat, when a

small quantity of a dark flocculent substance usually remains; the alcoholic solution is filtered whilst hot, and allowed to cool as gradually as possible.

Nitroharmidine is of a sulphur-yellow colour; it is very sparingly soluble in water at ordinary temperatures, when that fluid is poured over the alkaloid crystallized from alcohol; but when boiled with water and filtered whilst hot, the fluid becomes turbid during cooling by the separation of a portion of the alkaloid in very fine needles, so that nitroharmidine is much more soluble in hot water than in cold. For this reason, also, when the solution of a salt of nitroharmidine is precipitated by ammonia at a boiling heat, a portion of the alkaloid remains dissolved in the fluid, and is only partially deposited on cooling; whence, in this case, as in the alkaloids already treated of, the quantity of the alkaloid appears too small. The author adds, with regard to the precipitation of the salts of nitroharmidine by alkalies, that the alkaloid is separated from cold watery solutions in yellow gelatinous flakes, which exhibit no trace of crystallization, but which, when left for a considerable time in the alkaline fluid from which they were precipitated, are gradually converted into needles. In the fluid precipitated by ammonia, which has a pale yellow colour, the author found that this conversion had only taken place to a small extent in twenty-four hours, although tolerably large needles were formed; but in the solution which had been precipitated by potash, which was of a more or less deep orange-red colour, all the flakes were converted into extremely fine needles in the same time.

When nitroharmidine is put upon the tongue in small quantities, it is tasteless, probably in consequence of its slight solubility in water; its salts possess a slight bitter taste.

Nitroharmidine dissolves in much greater quantity in hot than in cold alcohol, as indeed appears from the above-described method of preparation. If the separation of the alkaloid be observed in a drop of the hot solution put upon a glass plate, the formation of distinct recognizable octahedra is frequently first remarked; these possess a darker yellow colour than the needles which afterwards make their appearance. The formation of these octahedra is caused by the rapid cooling of the fluid, and they are also obtained when a small quantity of a hot alcoholic solution is put into a test-tube, immersed in ice-water, and cooled as quickly as possible by moving it about. A pulverulent precipitate is then first formed, consisting of octahedric crystals swimming in the fluid, but the formation of acicular crystals very soon begins, even when the temperature of the fluid undergoes no change; in consequence of this the octahedra gradually disappear, so that at last nothing but acicular crystals are to be found. When it was attempted to filter the fluid immediately after the separation of the octahedra, and before the needles made their appearance, a formation of the latter always took place even during filtration, together with at all events a partial transition of the octahedra to the same form. Nitroharmidine is therefore apparently dimorphous.

Nitroharmidine is but sparingly soluble in æther; its cold, saturated, alcoholic solution is not precipitated by æther.

In boiling coal-tar naphtha (both in its most and least volatile constituents), nitroharmidine is soluble in considerable quantity; the greater part of it separates again, on the cooling of the solution, in acicular crystals, so that naphtha may serve equally well for its recrystallization as alcohol.

Nitroharmidine is soluble in tolerable quantity in petroleum at a boiling heat; on cooling, it separates so completely, if the alkaloid be perfectly pure, that the petroleum appears quite colourless, and only retains traces of the alkaloid in solution. The crystals consist partly of similar needles to those obtained from alcohol, but the author also observed short laminar prisms. The author did not obtain a crystalline compound of petroleum with nitroharmidine.

Nitroharmidine, even when boiled with solution of muriate of ammonia, only expels ammonia sparingly and slowly. With acids it forms pale yellow salts. Analysis gave:—

Carbon	60·83	60·77	26 =	1953·12	60·74
Hydrogen	4·19	4·26	22	137·28	4·27
Nitrogen	16·00		6	525·18	16·33
Oxygen.....	..		6	600·00	18·66

Nitroharmidine therefore is only distinguished from nitroharmalidine by the fact that 2 equivs. of hydrogen have been removed from it by the further action of the nitric acid; and as nitroharmalidine is to be regarded as harmaline in which 1 equiv. of hydrogen is replaced by NO^4, nitroharmidine may be considered as standing in the same relation to harmine, although, according to the author's experience, it cannot be produced from that body. According to the views of Berzelius, nitroharmidine is to be regarded as nitrite of oxide of harmidene and ammonia; its rational formula would then be $(C^{26} H^{16} N^4 O^3 + NO^4) NH^3$, and its symbol *nihd*Ak.

Muriate of Nitroharmidine is most readily obtained in the solid form in the way already described for the preparation of the alkaloid, *i. e.* when an excess of concentrated muriatic acid is added to a solution of the alkaloid in acetic acid, or to one prepared by heat with a few drops of muriatic acid. Muriate of nitroharmidine is soluble with difficulty even in dilute muriatic acid, and consequently soon begins to separate in fine needles; this separation increases rapidly, until, when the solution is tolerably concentrated, the whole sets into a gelatinous magma, which is to be put upon a filter, and washed with dilute muriatic acid to free it from any foreign matters which might be contained in the mother-liquor. The filter is then pressed between blotting-paper, the salt dissolved in boiling alcohol, and the solution digested with animal charcoal, then filtered and left to cool, when the salt shoots into acicular crystals with only a slight yellowish colour. The salt, prepared with the greatest care in this manner, and dried at the temperature of the atmosphere over sulphuric acid, contained 10·78 per cent. of water. It has consequently the following composition:—

Nitroharmidine.....	1	=	3215·58	78·02
Muriatic acid	1		455·76	11·06
Water	4		449·92	10·92

Muriate of nitroharmidine forms with chloride of platinum a double salt, which is obtained in acicular or laminar prisms, when a solution of chloride of platinum is dropped into a boiling dilute solution of muriate of nitroharmidine. The double salt is so difficult of solution, that on the boiling filtered fluid cooling, no more of the salt separates.

With bichloride of mercury a double salt is also formed, which separates in gelatinous flakes when the cold solutions are mixed. If, on the contrary, very dilute boiling solutions be mixed together, they remain clear, and it is only on the cooling of the solution that a double salt is deposited in the form of fine, microscopic, pale yellow needles, united in tufts.

Hydrobromate of Nitroharmidine is obtained by adding a solution of bromide of potassium or sodium to a solution of the acetate of the alkaloid, when, according to the concentration of the solutions, the salt separates either immediately or after standing for some time, in yellow silky needles.

Hydriodate of Nitroharmidine is formed like the preceding salt; but under certain circumstances, not yet exactly investigated, the separation of a brownish gelatinous body takes place simultaneously with the formation of the salt. This body is probably a compound of iodine with nitroharmidine, which will be described hereafter.

Hydrocyanate of Nitroharmidine.—The author did not succeed in forming a compound of hydrocyanic acid with nitroharmidine, like those with harmaline and nitroharmalidine; but hydrocyanate of nitroharmidine forms very permanent double salts with protocyanide and percyanide of iron. The combination with the protocyanide separates in gelatinous flakes on the mixture of the cold concentrated solutions; but if a solution of protocyanide of potassium and iron be dropped into a boiling solution of a salt of nitroharmidine, or into a cold but very dilute acid solution of a similar salt, the double compound separates in pale brown, prismatic, microscopic crystals, which are but sparingly soluble even in boiling water. The double salt of the percyanide is obtained in the same manner by the employment of the percyanide of potassium and iron; it is however much more soluble in boiling water than the salt of the protocyanide, and separates only on the cooling of the solution in yellow granular crystals. Hydrocyanate of nitroharmidine also forms a double salt with cyanide of mercury, when boiling solutions of acetate of nitroharmidine and of cyanide of mercury are mixed together. The double salt separates in yellow prismatic crystals on the cooling of the fluid. If ammonia be added to the mother-liquor filtered from these crystals, a voluminous flocculent precipitate is formed, which, when the precipitation is carried on at a boiling heat, takes the form of fine pale yellow needles. The various analyses of this substance did not agree well together; the author obtained 23–27 per cent. of peroxide of mercury.

Sulphocyanate of Nitroharmidine separates on the mixture of cold diluted solutions of salts of nitroharmidine and of sulphocyanide of potassium, in extremely fine, nearly colourless, acicular crystals; hot solutions remain clear, and deposit very long hair-like crystals only on cooling.

Sulphate of Nitroharmidine.—1. *Neutral Salt.* This is obtained by stirring the freshly-precipitated alkaloid with warm water, and adding to the mixture a quantity of sulphuric acid not sufficient for complete solution; the fluid is filtered and cooled, when the salt separates in pale yellow acicular crystals. 2. *Acid Salt.* If a great excess of concentrated sulphuric acid be added to the mother-liquor filtered from the neutral salt, and the fluid, which becomes heated, be set aside to cool, the salt crystallizes in pale yellow needles.

Nitrate of Nitroharmidine is difficult of solution in water, but still more so in dilute nitric acid; from which circumstance all solutions of other salts of nitroharmidine are very soon precipitated by nitric acid. The salt usually separates first in very pale yellow needles, which, however, when left in the fluid, are gradually converted into granular rhombohedric crystals of a darker yellow colour. A peculiarly crystallized product is obtained when the freshly-precipitated alkaloid is mixed with cold water, and small quantities of nitric acid, not sufficient for solution, are dropped into the mixture; afterwards carefully adding dilute ammonia until the alkaloid begins to separate, filtering the fluid, and leaving it to stand. In this manner a small quantity of a deep yellow substance is gradually deposited, which appears under the microscope to consist of long twisted and matted bands, arranged in tufts round a common centre. If extremely diluted ammonia be again dropped, and stirred into the fluid filtered from these until it has become permanently turbid, without however any perceptible precipitate being produced, a fresh quantity of this band-like body separates when the fluid is allowed to stand. This substance is somewhat soluble in water, and appears to be a basic nitrate of nitroharmidine. At ordinary temperatures it is unchanged either by ammonia or by solution of caustic potash, which is probably to be ascribed to its slight solubility in water; but with the aid of heat it is converted by alkaline fluids into acicular crystals. It is tolerably soluble in hot alcohol, and separates again, at all events partially, unchanged during and after the cooling of the solution, although not in so characteristic a form as when it is obtained from its watery solution

Acetate of Nitroharmidine.—If nitroharmidine be dissolved in a boiling mixture of acetic acid and alcohol, in which it is readily soluble, and the solution be left standing for some time, yellow, transparent, regular (octahedric?) and well-formed crystals are produced, which consist of a compound of the alkaloid with acetic acid. These crystals become dull, even by washing with water, after they are taken out of the mother-liquor, and when allowed to lie long in the water they gradually become decomposed, a part of them being dissolved and nitroharmidine separated. When they are boiled with water, this decomposition goes on rapidly throughout the whole mass

of crystals, which then, although partially retaining their external form, become converted into a multitude of fine needles of nitroharmidine. Connected with this decomposition of the acetate, which reminds us of the resolution of many metallic salts into acid and basic compounds, is the circumstance that when a watery solution of acetate of nitroharmidine is evaporated by heat, the alkaloid separates in acicular crystals, as soon as the solution has attained a certain degree of concentration. A similar phænomenon occurs with harmine.

Chromate of Nitroharmidine.—Solutions of salts of nitroharmidine furnish crystalline precipitates both with neutral and acid chromate of potash; these precipitates, when heated in the dry state, exhibit the same phænomena which the author has described in the case of chromate of harmaline. The result of this decomposition is a yellow alkaloid, distinct from nitroharmidine, but which the author has hitherto obtained in too small quantities to enable him to make any further examination of it.

Nitroharmidine and Oxide of Silver.—Oxide of silver forms a compound with nitroharmidine; it is very similar to that produced with nitroharmalidine. It is obtained in the form of a dark orange-red, somewhat transparent jelly, when a solution of silver is added to a perfectly neutral solution of nitrate of nitroharmidine; the solution of silver is prepared in the manner described for the corresponding compound of nitroharmalidine. Like the latter, this jelly also contracts on drying into solid, brownish-red, amorphous fragments, which present a considerable resemblance in their appearance to the so-called compact amorphous phosphorus.

Iodide of Nitroharmidine.—Nitroharmidine may be directly combined with iodine, without undergoing any change in its composition. The iodide of nitroharmidine thus produced furnishes a new example of the class of compounds discovered many years since by Pelletier; it is the more interesting, because on the one hand no subordinate products play any part in its formation, but on the other hand the new body may very easily be completely resolved into iodine and unchanged nitroharmidine. This substance is obtained by mixing together solutions of nitroharmidine and iodine in alcohol or naphtha; even when the solutions are boiling, a separation of a crystalline product immediately takes place. The best mode of proceeding is to add a solution of iodine in naphtha to a solution of the alkaloid in the same fluid until there is an excess of iodine, which may be known by the purple-red colour acquired by the fluid; this is then immediately filtered, and the filtrate washed with naphtha. The iodide of nitroharmalidine thus produced forms a loose woolly mass of microscopic needles of a yellowish-brown colour; it is as good as insoluble in cold alcohol, æther and naphtha, and is but very sparingly soluble even by heat. It may be heated to 212° F. without decomposition, both in the dry state and in water; but when boiled for a considerable time in alcohol, it is completely decomposed by degrees, a small quantity of iodine escaping along with the alcoholic vapours, whilst nitroharmidine

is set free. This resolution into iodine and alkaloid takes place much more rapidly and perfectly when the compound is boiled with dilute sulphuric acid; the whole then dissolves, forming a brownish-yellow fluid, and all the iodine soon escapes, exhibiting the characteristic colour of its fumes, whilst nothing remains in the solution but pure sulphate of nitroharmidine with an excess of sulphuric acid. The author made use of this property in analysing the compound; he obtained the following result:—

Nitroharmidine	..	..	1 =	3215·58	50·34
Iodine.....	48·58	48·82	2	3171·98	49·66

In a synthetic experiment made by the author with equivalents of nitroharmidine and iodine, he obtained a quantity of iodide of nitroharmidine nearly corresponding to theory; and this is a further proof of the correctness of the above proportion, as also that no subordinate products play any part in the formation of iodide of nitroharmidine.

Iodide of nitroharmidine appears to act as a base with muriatic acid; thus when this acid is poured upon it, it instantaneously acquires a black colour, and the microscope shows that the needles of the iodide of nitroharmidine have become covered with very much finer acicular crystals of a dark-coloured compound. When put into a drop of the acid upon a glass plate, iodine soon evaporates, and at length nothing, or scarcely anything but muriate of nitroharmidine is left; this reminds one of the similar behaviour of hydrocyanide of harmaline. If muriatic acid and alcohol be poured upon nitroharmidine, the latter is readily dissolved by the aid of heat, forming a dark yellow fluid, which on cooling becomes nearly solid from the separation of extremely fine, long, hair-like, black, microscopic crystals. A crystalline product, partly in an acicular form and partly in the form of roundish grains, in both of a black colour, is also obtained when an alcoholic solution of iodine is added to an alcoholic solution of muriate of nitroharmidine: but whether these black products be really the muriate of iodide of nitroharmidine, or whether they belong to another class of bodies, can only be shown by a further complete investigation of iodide of nitroharmidine, which is so interesting in many respects; for this however the author had not at the moment the necessary materials. No analogous compounds have yet been produced with other acids.

The behaviour of iodide of nitroharmidine with hydrocyanic and acetic acids is worthy of notice. It dissolves in considerable quantity in a concentrated alcoholic solution of hydrocyanic acid even at ordinary temperatures, forming a solution with only a slight yellowish colour; when a drop of this is evaporated on a glass plate, a reddish-brown crystalline body is separated, which the author is inclined to regard as unchanged iodide of nitroharmidine. But if a saturated solution be prepared by the assistance of heat, prismatic crystals of a ruby colour, and by no means of microscopic size, are formed in it on cooling; and these, as was shown by an analysis effected in the manner already described, contained a much smaller

quantity of iodine. These crystals therefore evidently consist of quite a different body, which, like that obtained on the evaporation of the hydrocyanic acid, requires further examination. Boiling concentrated acetic acid also dissolves iodide of nitroharmidine abundantly, forming a brown solution, from which dark-coloured crystals separate on cooling.

Bromine and chlorine do not appear to combine directly with nitroharmidine; they exercise a decomposing action upon it, and products are formed, which the author will describe in a separate paper.—*Bull. de St. Pétersb. Classe Physic-Math.*, xii. p. 33.

Upon some Compounds of Stibæthyle. *By* Prof. C. Löwig.

Antimonite of Stibæthyle.—When an ætherial solution of stibæthyle is allowed to evaporate spontaneously, and the oxide of stibæthyle formed is extracted from the residue by a mixture of æther and alcohol, a white pulverulent amorphous body is left, which was formerly called æthylstibæthylic acid by the author. The white fumes which stibæthyle diffuses in the air before it ignites consist almost entirely of this compound. The author has also stated, in his 'Elements of Organic Chemistry,' that this body is a compound of $(St.Ae^3)O^2+2StO^3$. The analysis of the compound, dried at 212° F., gave—

Stibæthyle	68·33	69·04
Carbon	12·58	12·67
Hydrogen	2·70	2·77
Oxygen	..	..

These results admit of three formulæ,—1st, $(StAe)O^3$; or 2nd, $(StAe^3)O^2$, $2StO^4$; or 3rd, $(StAe^3)O^2$, $2StO^3$.

It appears that the compound contains oxide of stibæthyle, and consequently that the first formula cannot be appropriate; for muriatic acid immediately separates a colourless fluid from its alcoholic solution, and this, when dissolved in alcohol, is not precipitated by sulphuretted hydrogen. This substance contains 24·60 chlorine. The muriatic acid solution separated from this chloride of stibæthyle furnishes kermes immediately with sulphuretted hydrogen, and when mixed with water gives algaroth powder.

Moreover, if the compound be digested with dilute nitric acid and evaporated, crystals of nitrate of stibæthyle are obtained, and the undissolved portion evolves no oxygen gas. It must consequently contain oxide of stibæthyle and oxide of antimony. It has a bitter taste, resembles sulphate of quinine, and is soluble in water and alcohol. The watery solution, when prepared cold, becomes thick, like starch-paste, when heated, and dries into a white porcelain-like mass. When water is poured over it, it leaves some oxide of antimony.

Sulphantimonite of Stibæthyle, $(St.Ae^3)S^2+2StS^3$.—The watery solution of the preceding compound furnishes a pale yellow precipitate with sulphuretted hydrogen, which resembles sulphuret of

arsenic; it has an extremely unpleasant and very persistent odour, like mercaptan. When dried over sulphuric acid, it forms a beautiful pale yellow powder, which, when heated on the water-bath, acquires a brownish-red colour. Fuming nitric acid decomposes this compound with production of flame; if it be distilled, a fluid product is obtained, which possesses the properties of sulphuret of æthyle. If dilute sulphuric acid be poured over it, kermes is separated, with evolution of sulphuretted hydrogen, whilst sulphate of stibæthyle is formed. Analysis gave:—

Stibæthyle	..	..	3 =	387	64·28
Carbon.....	11·68	..	12	72	11·96
Hydrogen	2·59	..	15	15	2·49
Sulphur	20·70	20·78	8	128	21·27

The same compound is also produced when an excess of solution of sulphuret of stibæthyle, $(StAe^3)S^2$, is treated with freshly-precipitated kermes.—*Journ. für Prakt. Chem.*, lx. p. 352.

On Methplumbæthyle. *By* Prof. C. Löwig.

An alloy of 1 part of sodium with 6 parts of lead reacts briskly upon iodide of æthyle. When the reaction is ended, if the mass be agitated with æther, and the æther afterwards allowed to evaporate in the absence of air, there remains a mixture of several fluid radicals containing lead. These have but little odour; they are insoluble in water, but readily soluble in alcohol and æther. They do not fume in the air, but burn, when ignited, with evolution of vapours of oxide of lead. They ignite when concentrated nitric acid is poured over them, and explode violently when brought into contact with iodine or bromine. If the solution in æther or alcohol be allowed to evaporate in the air, a white amorphous powder is deposited, which is insoluble in water, alcohol and æther, and forms crystallizable salts with acids; the solution contains a strong base, oxide of methplumbæthyle. The radical of this oxide is the principal product of the action of iodide of æthyle upon the alloy of lead and sodium.

Methplumbæthyle has the constitution Pb^2Ae^3.

Oxide of Methplumbæthyle, $(Pb^2Ae^3)O$, is prepared by adding to the alcoholic solution of the radical a solution of nitrate of silver to which alcohol has been added until no more metallic silver is precipitated. The solution now contains nitrate of oxide of methplumbæthyle. This solution is now agitated with alcoholic solution of potash, and afterwards with æther. Water is then added until the ætherial solution of the base is deposited; the æther is then distilled off, when the hydrate of oxide of methplumbæthyle is obtained as an oleaginous fluid, which afterwards solidifies in crystals.

It is readily soluble in alcohol and æther, but difficult of solution in water; it is volatile, and a glass rod moistened with it emits fumes. When heated, it forms white fumes, which produce sneezing. The solutions are strongly alkaline, with an acrid taste, leaving an

unpleasant sensation in the throat. It has a slippery feel, like hydrate of potash.

The composition of the pure oxide is—

Lead	2 = 208		69·07
Carbon	12	72	23·92
Hydrogen	15	15	4·98
Oxygen	1	8	2·03

Carbonate of Methplumbæthyle, $(Pb^2\ Ae^3)\ O, CO^2$, is formed when the alcoholic solution of the oxide is exposed to the air. It forms small, shining, hard crystals. It is insoluble in water, and difficult of solution in alcohol and æther. Alcohol containing muriatic acid dissolves it with effervescence. It has a strong burning taste, and behaves in general like the carbonate of an alkali. Composition :—

Lead	63·87	63·74	2 = 208		64·00
Carbon	23·93	23·40	13	78	24·00
Hydrogen	4·74	5·00	15	15	4·62
Oxygen	7·46	7·86	3	24	7·38

Sulphate of Methplumbæthyle, $(Pb^2\ Ae^3)\ O, SO^3$, is precipitated from the alcoholic solution of the oxide on the addition of sulphuric acid; the base must be in excess. This salt is insoluble in water, absolute alcohol and æther, but dissolves readily in alcohol containing muriatic acid. Sulphuric acid has the same effect, and the salt crystallizes from the acid solution in rather large, shining, hard, octahedric crystals. Analysis gave—

Lead	61·40	60·30	2 = 208		60·60
Carbon.....	20·30	20·33	12	72	20·90
Hydrogen	4·48	4·60	15	15	4·30
Oxygen	2·08	3·10	1	8	2·54
Sulphuric acid....	11·74	11·67	1	40	11·66

Nitrate of Methplumbæthyle, $(Pb^2\ Ae^3)\ O, NO^5$.—The preparation of the alcoholic solution of this salt has already been given. If this be evaporated upon the water-bath until it forms a thick oil, the residue afterwards becomes solid in a crystalline form. It is readily soluble in alcohol and æther, and when heated is decomposed with a slight explosion. It contained 14·65 and 14·89 per cent. of nitric acid.

Chloride of Methplumbæthyle, $(Pb^2\ Ae^3)\ Cl$, is obtained by the mutual decomposition of the sulphate of methplumbæthyle dissolved in alcohol and chloride of barium. It is extracted by means of æther; the ætherial solution is then separated by the addition of water, and allowed to evaporate.

It forms fine shining needles, which are readily soluble in æther and alcohol. When heated, it smells like oil of mustard. It explodes slightly even when gently heated, chloride of lead and metallic lead being formed. Analysis—

Lead.....	62·66	62·74	2 =	208	62·93
Carbon.....	21·68	21·51	12	72	21·78
Hydrogen.....	4·85	4·71	15	15	4·56
Chlorine	10·54	10·58	1	35·5	10·73

Bromide of Methplumbæthyle, $(Pb^2 Ae^3) Br$.—Sulphate of methplumbæthyle is dissolved in alcohol acidulated with sulphuric acid, and an alcoholic solution of bromide of potassium is added to the solution. The bromide is very like the preceding salt, and crystallizes in long needles; it contained 20·98 and 21·23 per cent. of bromine (calculated 21·33).

Iodide of Methplumbæthyle, $(Pb^2 Ae^3) I^3$, is produced like the preceding salt, substituting iodide for bromide of potassium. The solution is decomposed however when allowed to evaporate spontaneously, iodide of lead being separated. When evaporated rapidly, it is less decomposed; and if the undecomposed portion be distilled with water, iodide of lead is immediately deposited; but a colourless fluid passes over with the watery vapour, and this is no longer subject to spontaneous decomposition. It has an extremely penetrating odour, like oil of mustard, and furnished on analysis—

Lead.....	36·58	4 =	416	36·40
Carbon.....	25·11	48	288	25·02
Hydrogen.....	5·70	60	60	5·24
Iodine	34·16	3	381	33·34

Journ. für Prakt. Chem., lx. p. 304.

On the presence of small quantities of Copper in the Animal Organism. *By* H. Wackenroder.

In a detailed memoir, the author has submitted the various statements respecting the occurrence of copper in the human body to a critical examination, concluding with the results obtained in an examination of the blood for copper.

The method of treatment adopted is that already described by the author for forensic investigations. But when, as in the present case, the question relates to very small quantities, the following circumstances must be borne in mind.

When the blood, in which the presence of copper or other metals is to be ascertained, is treated with chlorine, it is very slowly decomposed. If, however, it be beaten up with a common whisk, so as to divide the coagulated masses, as much as 8 oz. of blood may be completely converted, in the course of a few hours, into a yellowish-white voluminous mass, just like albumen precipitated by muriatic acid. The filtration of the fluid, which has only a pale yellowish tinge, now takes place rapidly through a filter which has been washed with muriatic acid; the voluminous contents of the filter however require rather long washing, so as not to lose too much of the fluid. The white mass diminishes greatly in volume when dried, and forms a yellowish-white transparent mass, not unlike dried white of egg.

If diluted muriatic acid be employed, with successive additions of small quantities of chlorate of potash, the decomposition, and even nearly complete solution of the blood is effected by boiling in a porcelain dish for a quarter or half an hour. Boiling with muriatic acid containing free chlorine not only dissolves blood-clot, which is acted upon with so much difficulty by the watery solution of chlorine, but also other soft parts of animals and proteine substances, such as flesh, snails and frogs, leaving a scarcely observable residue.

There is therefore no difficulty in determining which means of decomposition should be preferred. There nevertheless remains one circumstance to be taken into consideration, namely, that the simple chlorine forms a fluid which contains less free muriatic acid and a smaller quantity of dissolved proteine substances than that produced by muriatic acid and chlorate of potash. It consequently requires less dilution and less treatment with sulphurous acid than the latter. These advantages cannot however as a general rule compensate for the troublesome decomposition of the blood by pure chlorine. Both fluids must always be sufficiently diluted to allow every trace of copper and lead to be precipitated by the passage of sulphuretted hydrogen.

The clear fluid obtained would always furnish with sulphuretted hydrogen a more or less copious precipitate of sulphur and organic substances, unless sulphurous acid gas be first passed into it in excess, and the fluid afterwards heated to expel the sulphurous acid. This is especially the case with the fluid prepared with muriatic acid and chlorine. In these sulphurous precipitates the presence of traces of the sulphurets of copper or lead is not readily determined with certainty.

The quantities of these are usually so small, that they can only be determined by the reduction of the metals from the ashes of the filter. This is burnt as completely as possible between the forceps in the air; the carbonaceous residue is then moderately heated in a platinum or porcelain crucible until the coal is completely burnt. In making use of a platinum crucible, however, all scraping of the platinum with a wire or otherwise must be avoided, as, if particles of this metal be rubbed off, they may readily lead to errors.

The ashes of the filter are worked up into a paste with some pure carbonate of soda and a little water, which is best done in the palm of the hand. This is then exposed on charcoal to a good reduction-flame before the blowpipe. Sometimes a white coating of volatilized alkaline salts is produced; this must be carefully distinguished from the pale yellow coating of oxide of lead. The ash of the charcoal, which always occurs, is readily recognizable under a tolerably strong lens.

As the ashes of the filter always contain sulphates, when they are heated to redness with soda, sulphuret of sodium is always produced, whence the calcined ash acquires a red colour. The sulphuret of sodium however prevents the complete separation of the sulphur from the copper and lead, when only traces of these metals are present. But if a little nitrate of potash be added to the strongly heated

mass of salts, and the flame be reapplied, complete reduction of the metals takes place, and even the smallest traces of them may be recognized by subsequent washing.

The following substances have been examined for copper by my pupils,—Dörr, Petzoldt, Schmeisser, Hartung and Gräfe.

The clot of a cup of venous blood, taken from an adult at the commencement of a state of plethora, the health otherwise being good, was decomposed by chlorine (by Dörr), and the fluid obtained submitted to the further treatment just described. The ashes of the filter were heated to redness on charcoal by the blowpipe with soda and nitrate of potash. By washing, very distinct shining red scales of metallic copper were obtained.

A similar quantity of clot from the same blood was decomposed by dilute muriatic acid with a little chlorate of potash, and almost entirely dissolved.

The ashes of one-half of the filter were heated to redness on charcoal by the blowpipe, merely with the addition of soda. On washing, only a black, undistinguishable and doubtful metallic powder was obtained.

The ashes of the other half of the filter, on the other hand, were exposed, with the addition first of soda and then of a little nitrate of potash, to the action of a good reduction-flame on charcoal; in this manner perfect laminæ of copper were obtained. The presence of no inconsiderable quantity of copper in this blood was consequently placed beyond a doubt.

Three cups of venous blood, taken from a young full-blooded man, who had fallen into a state of stupor, apparently in consequence of violent exertion and overheating himself on the previous day, were decomposed by chlorine. When the ashes of the filter were heated with soda by the blowpipe to a red heat on charcoal, a distinct coating of oxide of lead was observed; and after heating with a little nitrate of potash, washing separated a soft white metal, with here and there a reddish tinge. The scales of metal were insoluble in cold concentrated muriatic acid, but disappeared rapidly in concentrated nitric acid. As the second half of the ashes of the filter, which had been reserved, furnished the same result, it may safely be assumed that this blood contained traces of lead, but perhaps no copper. When the fluid was rendered ammoniacal, repeatedly treated with sulphuretted hydrogen, and again acidified, minute traces of lead could still be separated.

Seven ounces of sheep's blood, carefully collected, were decomposed and dissolved by muriatic acid and chlorate of potash. The ashes of the filter gave no traces of copper or lead. From the precipitate subsequently obtained from the fluid, when rendered alkaline, treated with sulphuretted hydrogen, and then again acidified, only scales of iron could be obtained; these had acquired a certain degree of lustre by trituration in the agate mortar.

Schmeisser also only detected a trace of copper or lead in 8 oz. of ox-blood; the ignition of the ashes of the filter was effected at twice, and thus checked.

About 3 oz. of fowls' blood was decomposed by Dörr, with muriatic acid and chlorate of potash. The ashes of the filter only furnished traces of reduced iron, but no copper or lead.

From the examination of the three last kinds of blood, it would appear that the blood of purely vegetable-feeding animals contains neither copper nor lead, or contains them in quantities so small as not to be recognizable in small quantities of blood.

About 8 oz. of duck's blood were decomposed by Hartung with muriatic acid and chlorate of potash. The precipitate produced from the acid fluid by sulphuretted hydrogen, when reduced with soda and a little nitrate of potash, furnished, on being washed, a tolerable quantity of reddish-white, shining, metallic scales, which were insoluble in concentrated muriatic acid, but dissolved very rapidly in concentrated nitric acid; as, at the same time, no coating was observable on the charcoal, these must be regarded as copper, with which however a trace of sulphur, or perhaps even of iron, was mixed.

Eight snails were examined by Dörr. The animals were completely divested of their shells, and then boiled in dilute muriatic acid with some chlorate of potash; they dissolved in this with but little residue. Notwithstanding the employment of sulphurous acid, however, a small quantity of organic substance was gradually carried down during the precipitation by sulphuretted hydrogen. Hence also the fluid only filtered slowly, and again became turbid after filtration. The precipitate on the filter had a brownish-gray colour, and was strongly adhesive. The ashes of the filter were divided into two parts, and ignited in the reducing flame with soda, with the subsequent addition of a little nitrate of potash. Both reductions furnished apparently equal quantities of very shining red laminæ of copper, of which two, when examined by the lens, distinctly presented the appearance of flattened globules of reduced copper.

The acid fluid, when rendered ammoniacal, again treated with sulphuretted hydrogen and acidified, furnished a brownish precipitate. The ashes of the filter were however so rich in earths, that they only partially fused up with soda and nitrate of potash. Nevertheless even in this case some traces of copper were detected.

Lastly, an excess of ammonia was added to the residuary fluid, the rather voluminous precipitate collected and reduced to ashes, which were digested with muriatic acid. In this solution there was sufficient iron to show the presence of that metal in the entire body of the snail.

Sugar-candy was also tested for copper. Gräfe operated upon a quarter of a pound of this substance, and obtained traces of copper.

From these facts Wackenroder concludes,—

1. That domestic animals, which live upon pure vegetable food, have no copper in their blood, or at least not sufficient to render it observable in half a pound of blood.

2. That the blood of man and domestic animals, living upon mixed nourishment, may contain very considerable quantities of

copper, and sometimes also of lead. This presence of metal is however by no means to be regarded as constant or normal.

3. The origin of these small quantities of copper and lead can only be attributed to nutritive or medicinal substances containing these metals.

4. It is not probable that these portions of copper and lead, small though they be, can remain without any influence upon the human organism.

5. The bodies of many animals of the lower classes may, like the snails, constantly contain a proportionably large quantity of copper.

6. Very small quantities of copper and lead, found in forensic investigations in different parts of the human body, cannot always be regarded as signs of poisoning.—*Archiv der Pharm.*, lxxv. pp. 140 and 268, and lxxvi. p. 1.

On the Preparation of Pyromucic Acid. By M. Arppe.

The crude tar-like mass obtained by the distillation of mucic acid, after it has been dried on the water-bath, is treated in the apparatus recommended by Mohr for the preparation of benzoic acid. —*Ann. der Chem. und Pharm.*, lxxxvii. p. 238.

ANALYTICAL CHEMISTRY.

On the Estimation of Tin. By Peter Hart, *Manchester**.

In the last Number of the Chemical Society's Journal (April 1854) there is an article by Dr. Penny on the bichromate method, in which he recommends the addition of a protosalt of iron and sulphocyanide of potassium to the test, with a view to render distinct the point at which sufficient bichromate solution has been added; I must confess that in my hands, some months back, before the appearance of his paper, this was not very successful, but the contrary, so much so that I gave it up as having a tendency to render the operation more difficult than it otherwise would be.

I found that on each addition of the bichromate solution a quantity of sulphocyanide of iron was formed, which, while there was comparatively a large amount of protochloride of tin present, was easily reduced, but towards the close of the operation, when there was but a small quantity of protochloride present, required some time. I often found, after placing the flask on one side, supposing it finished, that in a few minutes the red colour had disappeared, and the solution remained of the ordinary green colour; on the addition of more bichromate solution it again became red, only to disappear

* Communicated by the Author.

again in a short time; and this would perhaps be repeated three or four times.

The process I propose, is to add to the dilute solution of protochloride of tin in the flask a small quantity of iodide of potassium solution and a little thin starch-paste; with this addition it will be found that one drop of the bichromate solution in excess will cause the contents of the flask to assume a strong blue colour, the chromic acid setting free a quantity of iodine, which combining with the starch present produces the blue iodide of starch.

This improvement, by means of which the veriest tyro, with common precautions, can estimate tin with as much exactness as the most practised person can by the bichromate process, will, I think, prove an acquisition to the student, and any one who may only occasionally have to test a solution of tin; for whatever may be said to the contrary, it is certain that considerable practice is requisite before precision can be attained by using the bichromate solution simply.

It must be borne in mind that this process does not remove the difficulty pointed out by Mr. Leishing, but that his objection to the simple bichromate test still holds good after the addition I propose; in short there must not be more than a trace of iron present, or the result is vitiated in a corresponding degree.

On the Detection of Strychnine in Saccharine Powders.
By A. Vogel, Jun.

Otto has recommended bichromate of potash as a test for strychnine. The substance to be tested is mixed with the finely-powdered salt, and then moistened with sulphuric acid; a dark violet colour is produced. Brieger states that strychnine mixed with sugar cannot be discovered in this way. The author says that in this case the substance to be tested must first be moistened with sulphuric acid, and the salt afterwards added to it. By adopting this plan, moreover, the reaction is not prevented either by quinine, cinchonine, starch or dextrine.—Buchner's *Neues Repert.*, ii. p. 560.

On a Modification of Vogel's *Test for Quinine.*
By M. von Klitzinsky.

Vogel's test does not always indicate quinine with certainty in organic fluids, as for instance in the urine. Under such circumstances the quinine must first be separated by an excess of calcined magnesia and evaporating the fluid therewith to dryness; the residue is extracted with a mixture of 1 part of alcohol and 2 parts of æther, and this extract evaporated to dryness, and the alkaloid extracted from it by means of æther. The æther now leaves tolerably pure quinine, which allows the reactions of the following series of operations to be recognized with more certainty.

Boiling water is saturated with ferridcyanide of potassium (instead of the ferrocyanide according to Vogel), and to the solution

whilst still hot five times its quantity of the strongest solution of chlorine is added; ammonia is then added to the blackish-green solution until it has a strong alkaline reaction; it is then filtered from the brown flakes of hydrated peroxide of iron which separate. This test-fluid cannot be kept long. The fluid to be tested for quinine is first mixed with an excess of solution of chlorine; the reagent is then dropped in, when the presence of quinine is indicated by the production of a beautiful blood-red or violet colour.—Buchner's *Neues Repert.*, ii. p. 567.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Uranium-yellow. By A. Patera.

The author has endeavoured to prepare the purest possible uranium-yellow directly from the pitch-blende of Joachimsthal, so as to enable it to be brought to market. More than 15 cwts. of uranium-yellow have been prepared by the author's method at Joachimsthal in the course of last year. The ore employed contains about 45 per cent. of protoperoxide of uranium, together with arsenic, antimony, sulphur, lead, bismuth, iron, manganese, zinc, nickel, cobalt, &c. in variable quantities.

The finely-powdered ore is roasted in the reverberatory furnace with finely-powdered limestone, until the protoperoxide of uranium is entirely converted into the compound of oxide of uranium and lime. This is readily soluble in diluted sulphuric acid. The solution is effected in wooden tubs, the whole being kept frequently stirred; it takes place so completely, that the residue, which was about half the weight of the mass employed, contained only 6 oz. of protoperoxide of uranium in the hundredweight, which scarcely represents one-half per cent.

The solution of sulphate of uranium, which has a beautiful green colour, is now mixed with a solution of carbonate of soda in water. By this the uranium is first of all precipitated, together with any small quantities of other metals and earths which may be contained in the solution; but an excess of the carbonate of soda redissolves the oxide of uranium tolerably free from impurities; a precipitate of iron, manganese, lime, &c. is left, which however still retains some oxide of uranium; this precipitate is again boiled with carbonate of soda and washed with water, when it only contains traces of uranium. Sulphuric acid is now added to the alkaline solution of oxide of uranium as long as an effervescence is observed; during this process the clear solution becomes turbid. The carbonate of soda and uranium is decomposed, and hydrated biuranate of soda separates; this is drained in linen bags, pressed and washed. The washed and dried product is then powdered, and put up in packets.

The salt thus obtained is extremely pure; it is constituted according to the formula Na, $2UO^3+6HO$; the same formula is obtained by the analysis of eliasite (Haidinger) and gummierz (Breithaupt), when the impurities are deducted. Gummierz contains lime instead of soda; eliasite, lime and magnesia.

The large quantity of uranium-yellow prepared by this method in Joachimsthal in the course of last year was much purer than that usually met with in commerce, and, according to the testimony of several glass-makers, was particularly fitted for the manufacture of yellow glass. It is certainly the first time that this scarce material has been really manufactured in such large quantities, as in the methods previously adopted the employment of concentrated nitric and sulphuric acids, and the consequent necessity of using porcelain and glass apparatus, only allowed small quantities of the ore to be operated upon, whilst in the process just described the ore is so completely decomposed by the preliminary roasting with lime, that it becomes soluble in dilute sulphuric acid, which allows the employment of wooden tubs, and facilitates its manufacture as an article of trade.—*Sitzungsber. der Akad. der Wiss. zu Wien, Math. Naturw. Kl.*, xi. p. 842.

On the Preparation of Copal Varnish. By Prof. Heeren.

There is no difficulty in dissolving copal in fatty and volatile oils when the resin has been previously fused; by this process, however, a more or less distinct coloration is produced, and the natural hardness of this fine resin is injured. It has therefore been often attempted to dissolve copal without previous fusion; but, as is well known to all who have occupied themselves with this question, great difficulties have been found in effecting the solution. Directions have been given to soak the pounded copal in æther or ammonia until it swells up into a gelatinous form, and then to dissolve it in strong alcohol; but this process never succeeded with the author, though he tried it repeatedly. Others recommend hanging the copal in a small bag in a retort, in which absolute alcohol is gently boiling. This method also failed, in the author's hands, in producing even a tolerably-concentrated varnish.

The best prescription appears to the author to be that given by Freudenvoll in his treatise on the preparation of varnishes. According to him, 4 oz. of West Indian copal are dissolved in a mixture of

4 oz. oil of turpentine, and
6 oz. alcohol of spec. grav. 0·813;

or a mixture of

4 oz. sulphuric æther,
4 oz. oil of turpentine, and
4 oz. alcohol of spec. grav. 0·851.

When engaged in testing this process, which gave very good

results, the author found a small variation, which he describes as follows, particularly efficacious:—

Two sorts of copal occur in commerce, the East and West Indian. The former is usually in small, irregular, rounded pieces, with a finely-verrucose surface, the resemblance of which to the skin of a goose has obtained for it the name of "goose copal." It is of a somewhat yellow colour, and is preferred for the manufacture of oily copal varnish, because it acquires less colour by fusion than the West Indian. The latter does not possess a warty surface; it is very pale in colour, often nearly colourless, and occurs in large irregular fragments, partly with a rounded surface and partly with a shelly fracture.

West Indian copal only can be employed in the following solution, the East Indian forming only gelatinous lumps, but never a solution. The solvent is a mixture of

60 parts by weight of alcohol of spec. grav. 0·813,
10 parts by weight of sulphuric æther,
40 parts by weight of oil of turpentine,

in which 60 parts of copal are to be dissolved for the production of a varnish of an oleaginous consistence. Solution takes place, even in the cold, without any previous gelatinous swelling of the copal; but it is effected much more rapidly with the assistance of a gentle heat. As, however, single pieces are often found in the West Indian copal, which instead of dissolving only swell up in the fluid, by which the rest of the solution is spoiled, it is advisable to select only the large and perfectly clear pieces for the purpose of varnish-making, and to test each first of all as to its solubility. This little trouble is richly repaid by the certainty of the result.

To test this quality, a small splinter of the copal is put into a small test-tube; a little of the solvent fluid is then poured in, and the whole is heated. If the copal dissolves completely in a few minutes without becoming gelatinous, it is good.

When the desired quantity of good copal has been got together in this manner, it is to be pounded to a tolerably fine powder, which is to be put into a glass retort or flask, the necessary quantity of the solvent added, and the whole heated and shaken until solution is effected. To clear the varnish, which may appear somewhat dull, from dust or other impurities, it may be allowed to stand a long while until these settle; or if it be desired to effect this quickly, it may be filtered through blotting-paper, placed as a filter in a glass funnel; the filter must not project above the edge of the funnel, so that the latter may be closed by a glass plate laid over it. The passage of the thick varnish is of course very slow, but the varnish is obtained perfectly clear in this manner; and if the copal employed were very clear, it is nearly colourless. It dries rapidly, but like all turpentine varnishes retains a slightly sticky surface for some days.—Dingler's *Polytech. Journ.*, cxxx. p. 424.

THE CHEMICAL GAZETTE.

No. CCLXXVIII.—May 15, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Theoretical Relations of Water and Hydrogen.
By T. S. Hunt, *Chemist to the Geological Commission of Canada.*

In carrying out his theory of types, M. Laurent proposed to consider water, $H^2 O^2$, having its equivalent represented by 4 vols. of vapour, as the type of the oxides like $M^2 O^2$, of the hydroxides $(MH)O^2$, and of the sulphurets corresponding to these two classes. By his system of compound radicals, Liebig had extended to organic chemistry the nomenclature of Lavoisier; and he looked upon spirit of wine, $C^4 H^6 O^2$, as the hydrated oxide of a radical æthyle ($C^4 H^5$ = Et), while hydric æther, $C^4 H^5 O$, was the simple oxide of the same radical. But as æther vapour contains in the same volume twice as much carbon as the vapour of alcohol, Gerhardt had already proposed to double the formula of æther, and Laurent now showed that while alcohol is to be regarded as the hydroxide of æthyle $(EtH)O^2$, or water in which æthyle replaces an equivalent of hydrogen, æther is the anhydrous oxide, in which the second equivalent of hydrogen is replaced, and should be written $Et^2 O^2$. Hence while æther is neutral, alcohol is monobasic, having an equivalent of hydrogen replaceable by a metal, and is the type of monobasic vinic acids, while water is the type of bibasic acids *.

In a review of that remarkable essay, published in Silliman's Journal for September 1848, I suggested that this view was "susceptible of still further extension, and that we may include in the same type all those saline combinations (acids) *which contain oxygen.*" I referred to the hypochlorites ClO, MO, as derivatives of the type $H^2 O^2$, in which Cl replaces H; being $(ClH)O^2$ and $(ClM)O^2$, while anhydrous hypochlorous acid is $Cl^2 O^2$, the result of a complete substitution. "In the same manner nitric acid, NHO^3, is a monobasic salt (*i. e.* acid), corresponding to water in which NO^2 is substituted for H, as in many organic compounds; we have then $(NO^2, H)O$ and $(NO^2 M)O$," or $(NO^4 H)O^2$ in the notation adopted above. "As an adaptation of this idea to bibasic compounds, sulphuric acid, $SH^2 O^4$, is to be regarded as water in which SHO^3 replaces H; thus $(SHO^3, H)O$. As the replacing elements contain an equivalent of hydrogen which is saline (*i. e.* replaceable by a

* Laurent, Récherches sur les Combinaisons azotées. Ann. de Chim. et de Phys., Nov. 1846.

metal), the acid is bibasic. When the hydrogen in SHO^3 is replaced by a metal, we have a class of acid sulphates like $(SKO^3, H)O$. The complete replacement of hydrogen in the original type yields $(SHO^3)^2 O$, which is the Nordhausen acid, commonly represented by $2SO^3, H^2 O$. This latter compound, as Gerhardt has shown, corresponds to the anhydrous bisulphate of potash.

"The tribasic acids may equally be reduced to the same type, if we conceive the elements which replace 1 equiv. of hydrogen to be bibasic instead of neutral or monobasic; phosphoric acid, $PH^3 O^4$, is $(PH^2 O^3, H)O$.

"The primitive saline type is then essentially bibasic, and is presented in its most elemental form in water, while the simplest type of the monobasic salt, which is a derivative of the last, is found in hypochlorous acid." (p. 174.) This view of the derivation of polybasic acids is illustrated by the bibasic sulphacetic, and the tribasic sulphosuccinic acid.

On page 177 we further remark, that "the binary molecule of the metals, hydrogen, chlorine, bromine, &c., will be seen to be the type of an immense number of combinations, embracing the various alloys and amalgams, the hydracids like hydrochloric acid, with their corresponding salts, and such compounds as ClBr and ClI, while ICl^5 is referable to a triple molecule of these elements represented by H^6; to this type belong the perchlorides of antimony, arsenic and phosphorus, while the corresponding trichlorides form a double molecule."

In a subsequent essay on chemical classification, read before the American Association for the Advancement of Science at Philadelphia, in September 1848, and published in Silliman's Journal for May and July 1849, we observed that the relation between alcohol and acetene is that which subsists between the two types $H^2 O^2$ and H^2, acetene being hydrogen in which æthyle replaces H, thus $C^4 H^5, H = C^4 H^6$, while hydrochloric æther is a chlorinized hydrocarbon corresponding to hydrochloric acid, so that having repeated what has been already cited as to the type H^2, we add,—"Moreover it follows from the relations of HCl to the chlorinized hydrocarbons, that it (H^2) is the type of all the hydrocarbons, as well as of the alkaloids, which may be described as amidized species of them, and are equally susceptible of substitutions by chlorine." It was also remarked, that "as many neutral oxygenized compounds, which do not possess the saline character, are still derivatives of acids which are referable to the type $H^2 O^2$, we may regard all oxygenized bodies as belonging to this type." "While nitric acid is NHO^3, or $(NO^2, H)O$, the result of the complete replacement of H by NO^2 will be $(NO^2)^2 O$, or the unknown dry nitric acid, homologue of the so-called anhydrous phosphoric and arsenic acids, which are equally $(PO^2)^2 O$, &c." (vol. viii. p. 92.)

One of the objects proposed in the essay just quoted, was a comparison of the views of Gerhardt and Liebig with regard to the formation of æthers, amides, and allied bodies. Gerhardt, in accordance with the electro-chemical theory of Berzelius, had con-

sidered the acids in these reactions to be electro-negative by their oxygen, while the alcohols, ammonia, and the hydrocarbons were electro-positive by their hydrogen, so that these bodies *minus* H^2 replaced O^2 in the acid*. To this view we objected that it leaves unexplained that change in the basic relations of the acid, which Liebig rightly understood when he compared the æthers to salts, and represented the acid as losing H, which is replaced by the elements of the alcohol *minus* HO^2. This theory, unlike that of Gerhardt, made the æthers of the hydracids enter into the same class with those of the oxacids; at the same time it did not include those bodies which are produced with the elimination of H^2O^2, by the action of oxygen acids upon ammonia and hydrocarbons, and which were recognized in Gerhardt's system as completely analogous to the æthers in the mode of their formation. Here the compound radical theory is found to be defective, although the analogy which forms its point of departure is correct. In concluding this comparison, we remarked that "we are led to recognize the view of Liebig, *apart from his ideas of dualism, and his theory of compound radicals*, as the one fundamentally true." (vol. vii. p. 405.)

In Silliman's Journal for March 1848 (vol. v. p. 265), we observed that the relation of wood-spirit to acetonitryle is the same as that of water to hydrocyanic acid, and that water differs from wood-spirit precisely as this last differs from spirit of wine, so that the relation of homology, recognized by Gerhardt in the compounds of carbon, is extended to water and hydrogen; for from the relations which we have asserted between H^2O^2 and H^2, it follows that while water is the homologue of the alcohols, hydrogen H^2 is the homologue of acetene C^4H^6, (EtH), and of formene C^2H^4, (MeH), which Frankland calls hydrides of æthyle and methyle, as well as of his zincomethyle C^2H^3, Zn. The bodies which he regards as the alcohol radicals are still homologues of hydrogen, the result of a complete substitution, and are $(C^2H^3)^2$, &c., like benzile $C^{28}H^{12}O^4$, which is Bz^2, while bitter-almond oil is BzH.

In Silliman's Journal for January 1850 (vol. ix. p. 65), this is again referred to, and we remark, that as water is to be regarded as the homologue of the alcohols, it follows from the principles already laid down, "that the æthers are homologous with their parent acids," a point which was illustrated by the action of the cyanic æthers with ammonia; while the volatile bases of Wurtz "sustain to their corresponding alcohols the same relation that ammonia does to water." In vol. xiii. p. 206, we repeat,—"Water is not only the analogue, but the strict homologue of the alcohols, so that the molecule H^2 is the equivalent (homologue) of C^4H^6 and its homologues, and H of æthyle and methyle (the hypothetical radicals)."

The question whether these homologues of hydrogen H^2 are to be regarded as the radicals of the alcohols and æthers has been discussed by Gerhardt, Hofmann, and others, but resolves itself into this,—Frankland's æthyle is to EtCl what Zn^2 is to ZnCl, and H^2

* Précis de Chimie Organique, vol. ii. p. 495.

to HCl; the metals hydrogen and chlorine always present a dualism in their reactions as marked as æthyle, kakodyle and cyanogen.

Williamson* has made a beautiful application of Laurent's theory of the alcohols. By the action of potassic alcohol, $(EtK)O^2$, upon hydriodic æther, EtI, he obtained KI and Et^2O^2, and by a similar process mixed æthers, such as $(EtMe)O^2$. He at the same time explained the theory of the ordinary æther process, as the reaction between sulphovinic acid, $S^2(EtH)O^8$, and $(EtH)O^2$, giving $S^2H^2O^8$ and Et^2O^2. Meanwhile Chancel, following out the same idea, announced almost simultaneously with Williamson the production of hydric æther by the distillation of sulphovinate of potash with potassic alcohol; by the reaction of oxalovinate with sulphomethylate of potash, he also obtained a mixed oxalic æther, $C^4(EtMe)O^8$, oxalic acid being $C^4H^2O^8$.

Still more recently Gerhardt has announced the production of a class of bodies, which he describes as the anhydrides of the monobasic organic acids. He had formerly regarded the production of anhydrides as characteristic of polybasic acids, because he would not admit the theoretical derivation of monobasic acids from a bibasic type, H^2O^2, the complete replacement of whose hydrogen should, as I have long ago shown, yield neutral anhydrides (like the anhydrous nitric acid since discovered), sustaining to the corresponding acids the relation of hydric æther to alcohol. According to the view which I advanced in 1848, acetic acid, $C^4H^4O^4$, was represented by $(C^4H^3O^2, H)O^2$, and the anhydride would be $(C^4H^3O^2)^2O^2 = C^8H^6O^6$, corresponding to 4 vols. of vapour. This body has been obtained by Gerhardt, as well as the butyric, valeric, benzoic and cinnamic anhydrides, besides mixed species analogous to the mixed æthers, such as the acetobenzoic anhydride, which contains the elements of 1 equiv. each of acetic and benzoic acids *minus* H^2O^2. These bodies are of coarse neutral, and regenerate acids by assimilating the elements of water.

The process by which these bodies are obtained is very instructive. When the perchloride of phosphorus, PCl^5, or the oxychloride, PO^2Cl^3, acts upon a salt like the acetate of potash, a body represented by $C^4H^3ClO^2$ is obtained, which bears the same relation to acetic acid that hydrochloric æther does to alcohol; by the action of this acetic chloride upon acetate of potash, chloride of potassium and anhydrous acetic acid are produced. Alcohol, $C^4H^6O^2$, being represented as $(EtH)O^2$, we may write the formula of acetic acid $(AcH)O^2$, $(C^4H^3O^2 = Ac)$, while the chloride is AcCl. This corresponds to hydrochloric or hydriodic æther, while acetate of potash, $(AcK)O^2$, is analogous to potassic alcohol. The process is then similar to that by which Williamson obtained hydric æther, $AcCl + (AcK)O^2 = KCl + Ac^2O^2$, or the anhydrous acid.

The reaction in all these cases is, as I have pointed out in the paper before quoted (vol. viii. p. 93), identical in essence with that between HCl and $(KH)O^2$, yielding an alkaline chloride, KCl, and

* Philosophical Magazine for November 1850.

water, H^2O^2, the prototype of all the above acids, æthers, alcohols and anhydrides. We have there also remarked that H^2O^2 is to be regarded as a derivative of hydrogen, H^2, and that it is often difficult to distinguish between the types. Thus, for example, the acetic chloride might be regarded as a chlorinized aldehyde, $(C^4H^3, Cl)O^2$, belonging to the second type, while its reactions permit us to compare it with the hydrochloric æthers of the type H^2. It must be kept in mind, that although the apparent dualism deduced from the results of chemical change is subject to but very simple variations in the elements, it is exhibited in so many different ways in the higher species, that we cannot assign an absolute value to any hypotheses based upon their changes.

I have been particular in again bringing forward these views, because they now belong to the history of chemical theory, and because after having maintained them alone since 1848, and having insisted upon them in various ways in my communications to Silliman's Journal, I now find them brought forward by Williamson, Brodie and Gerhardt. This latter chemist, in a paper presented to the French Academy in June 1852, and published in the 'Annales de Chimie et de Physique' for March 1853, abandons those theories to which I long since objected, and brings forward, with a similarity of thought and expression not to be mistaken, the views upon which I have here insisted.

Williamson, in a paper read before the British Association in July in 1851, has expressed the same ideas with regard to the typical relations of water, and is recognized by the English editor of Gmelin's Handbook (vol. vii. pp. 17 and 201) as the author of the theory. See also Brodie's lecture before the Royal Institution in May 1853, "On the Formation of Hydrogen and its Homologues*."

It is gratifying to find that the views which I have so long maintained are at last recognized by chemists, and are found productive of beautiful and important results; but it would be only just in these chemists to have admitted the priority, by three or four years, of my own published views, anticipating the brilliant series of discoveries which have served them as the basis of their generalizations.—Silliman's *Journal*, March 1854.

On Aluminium. *By* Prof. Wöhler, *in a Letter to* M. Dumas. *With Remarks by* M. Sainte-Claire Deville.

It appears that my last observations on aluminium, published in the 'Annalen der Chemie und Pharmacie,' liii. p. 422, are not known in France. I will therefore give an extract from my memoir, with the view of completing the history of this metal, and confirming the results obtained by M. Deville. After describing the mode of preparation (with chloride of potassium), I said,—

"Aluminium is obtained in the form of a gray powder. But in examining the mass more closely, it is seen to be composed of small fused globules, some of which are as large as a pin's head. It fol-

* Chem. Gaz., August 1, 1853.

lows therefore that aluminium is fusible at the temperature produced at the moment of reduction. Direct experiments have shown that this temperature is not very high. In fact, I have found that aluminium may be fused with borax by the ordinary blowpipe, but that its quantity gradually diminishes in the borax. Thus I did not succeed in fusing it with borax in a crucible at the temperature required for the fusion of cast iron. It had entirely disappeared; and the borax had acquired a brownish-black colour, probably owing to the reduction of boron.

"Fused aluminium has nearly the colour and lustre of tin. It is perfectly malleable. I obtained a leaf of it, flattened under the hammer, which was 10 millims. in length. It is slightly magnetic, according to the observations of MM. Poggendorff and Riess, to whom I gave this laminar specimen. Its density, determined with two globules of 0·032 grm., was 2·50; determined with the laminated aluminium, it was 2·67. At ordinary temperatures it does not decompose water, but at 212° F. it begins to evolve hydrogen gas. It is soluble, with evolution of hydrogen gas, in even a dilute solution of potash, and also in ammonia.

"A globule of aluminium placed in oxygen gas, may be fused without becoming oxidized beyond the surface; but when heated a little more strongly, it burns with a dazzling brilliancy, like tin. The alumina produced in this manner is fused.

"Aluminium does not reduce lead and silver from a solution of their nitrates; but when it is immersed in a solution of oxide of lead in potash, the lead is reduced in brilliant laminæ, in the same manner as by zinc. It also reduces tin in a solution of the protoxide in potash, and silver in a solution of one of its salts in ammonia. Silver, when reduced by aluminium, is deposited in a compact mass and not in crystals. Copper is reduced by aluminium from a solution of its sulphate. If zinc and aluminium be placed in contact in a solution of a salt of lead or silver, the metals are also deposited upon the aluminium."

I am extremely curious to learn the final results at which M. Deville may arrive. It would be a great advantage to science, and even perhaps for manufactures (as he himself hopes), if this distinguished chemist succeeds in effecting the reduction of aluminium by a more easy and œconomical process.

Letter from M. Deville *to* M. Dumas.

You have been good enough to communicate to me a letter from M. Wöhler, in which that illustrious chemist refers to his experiments on aluminium. Allow me to furnish you with some details, which may serve to elucidate this question completely.

The metal, which I obtained by means of sodium, but with an apparatus quite different from that hitherto employed, appears to me to differ essentially from the aluminium of M. Wöhler in the distinctness of its reactions. This difference is due to the presence of impurities, which it is impossible to avoid when operating with platinum vessels, even by employing the mode of operation recently

described by M. Wöhler. I have repeated his experiments with the greatest care, and, like him, I have obtained aluminium in the form of a gray powder; but with more attentive examination, some little metallic spheres, of a tin-white colour, may be observed with the naked eye; many of these are sometimes of the diameter of a pin's head.

Minute analyses have convinced me of the presence of sodium and platinum in this substance, the fusion of which is caused by the heat of the very lively reaction during which it is produced, and can never afterwards be effected by the blowpipe-flame. This temperature is very high, especially when compared with that which I employ in the fusion of aluminium, and which is intermediate between the points of fusion of zinc and silver. The presence of platinum* would explain this great difference.

The presence of sodium deprives the metal of most of its characteristic properties. Aluminium, according to M. Wöhler, decomposes water at 212° F., and dissolves in weak acids. Now a wire of aluminium, weighing 149·8 milligrms., was left for more than half an hour in contact with boiling water in a glass vessel; its surface was not tarnished, the water did not lose its limpidity, and the wire, when again placed in the scale, had lost none of its weight†.

Globules only weighing a few milligrammes remained nearly three months in weak sulphuric and nitric acid, without appearing to undergo any alteration. In boiling nitric acid, solution is effected so slowly, that I was obliged to renounce this mode of operation in my analyses. Lastly, if a globule of aluminium be allowed to fall upon caustic soda heated to redness and fused in a silver vessel, it resists even this powerful agent. The aluminium employed in these experiments, which had been analysed, was perfectly pure. It is upon these properties, together with the unalterability of the metal in the air, that I founded my hope that it is a metal which may become useful in the industrial arts.

Lastly, in operations carried on like those of M. Wöhler, the aluminium is obtained in microscopic globules, or at the utmost of the size of a pin's head, and their size depends upon chance; my method permits the formation of ingots of metal, the dimensions of which are only dependent on the quantity of substance submitted to experiment. It has been tried before several members of the Academy, and has never failed hitherto. I will also add, that the aluminium, which I now prepare by a new process, without the employment of any alkaline reducing agent, does not differ in any respect from that which I obtained in a state of purity by a modification of M. Wöhler's process.—*Comptes Rendus*, March 20, 1854, p. 555.

* At a low temperature aluminium acts upon platinum like mercury upon silver.

† Nearly all the bubbles of steam are formed upon the aluminium, which being very light is much agitated in the fluid; an evolution of hydrogen might readily be supposed. But the same appearances are produced, with still greater intensity, with a platinum wire, the metal remaining constantly at the bottom of the water.

Conversion of Thialdine into Leucine. By M. Gossmann.

Prof. Wöhler has announced that M. Gossmann has verified the relation supposed by M. Cahours to exist between thialdine and leucine. The former, $C^{12}H^{13}NS^4$, can be converted into leucine, $C^{12}H^{13}NC^4$, by treatment with oxide of silver and water at 212° F. —*Comptes Rendus*, March 20, 1854, p. 556.

On Lupuline. By J. Personne.

Lupuline is the yellow powder so readily obtained by rubbing the catkins of hops. To this powder the peculiar properties of the hops, their bitterness and aroma, are due. It has been investigated by D. Ivey of New York, and by Payen and Chevallier. (Also by Dr. Rudolph Wagner*.)

Lupuline furnishes both volatile and non-volatile bodies to boiling water. When distilled with water, an acid and an essential oil pass over as volatile constituents. The non-volatile substances are an organic acid and nitrogenous bitter matter, both of which are soluble in water. The author has not investigated these any further.

The *volatile acid*, determined by the analysis of the salts of silver, baryta and copper, is valerianic acid, of which lupuline contains about 1 per cent.

The *volatile oil* is lighter than water, becomes resinified in the air, and acquires acid properties. The boiling-point rises from 284° to 572° F. By fractional distillation, the author separated it into two different oils. One boils between 302°–320° F., the other at 572° F. Both have the constitution $C^{22}H^{18}O^2$; they turn the plane of polarization to the right, and do not solidify at 0° F. Concentrated sulphuric acid dissolves them with a red colour; they are again separated by water, and the sulphuric acid then furnishes with baryta a salt of a conjugate sulpho-acid; nitric acid converts them partly into resin and partly into valerianic acid. If let fall in drops upon hydrate of potash, they are converted into a hydrocarbon of the formula $C^{10}H^8$, with formation of carbonic and valerianic acids. If this hydrocarbon be deducted from the oil, $C^{22}H^{18}O^2 - C^{10}H^8 = C^{12}H^{10}O^2$, the latter expresses the valerole which Gerhardt prepared from valerianic acid. The hydrocarbon of the oil of hops however furnishes no Borneo camphor, and it also has a smell more like that of thymene.

The large quantity of resin contained in lupuline renders it difficult to obtain valerole from it. The solid resinous mass left after exhaustion with water consequently still contains much of this substance. If it be distilled with lime, taking care that it is not carbonized, Chancel's aldehyde of valerianic acid goes over; its composition is $C^{10}H^{10}O^2$. It boils at 194° F., and is rendered brown and resinous by potash, and very readily reduces salts of silver. Its specific gravity was 0·8009 at 68° F.—*Comptes Rendus*,

* See Chem. Gaz., vol. xi. p. 272.

On the Oil of Osmitopsis asteriscoides. *By* E. von Gorup-Besanez.

Martius received from Cape Town an oil denominated "essential oil of *Osmites Bellidiastrum*," accompanied by a specimen of the plant from which it had been obtained. This plant was determined by Schnitzlein to be *Osmitopsis asteriscoides*; it belongs to the family of Senecioid *Compositæ*.

The oil is a thin fluid, yellow with a tinge of green; it feels rough between the fingers, has a penetrating but not unpleasant odour, something like camphor and cajeput-oil, and a burning taste, somewhat acrid in the throat; it is neutral. Its specific gravity at 62°·15 F. is 0·931. It is insoluble in water, æther and alcohol; iodine dissolves in it without explosion; concentrated sulphuric acid gives it a brown colour; nitric acid thickens the oil, and produces a violent evolution of NO^4. Potassium becomes oxidized in it, with a slight evolution of gas. It furnishes no metallic speculum with an ammoniacal solution of silver, nor does it form a crystalline compound with alkaline sulphites. It is free from sulphur.

It began to boil at 350° F.; the boiling-point then rose to 354° F., and afterwards, between 370° and 404° F., a yellowish oil passed over; at 404°–408° F. a crystalline sublimate was formed in the neck of the retort.

The oil which passed over between 354° and 370° F. possessed a much finer odour than the original oil. A portion obtained by rectification, which boiled between 354° and 362° F., was analysed. Its spec. grav.=0·921.

The oil of the *Osmitopsis* is $C^{20}H^{18}O^2$, and consequently isomeric with Borneo camphor, cajeput-oil, &c., a relationship which Martius had already suspected. Analysis gave:—

Carbon	77·36	20	= 120	77·92
Hydrogen.....	11·53	18	18	11·69
Oxygen	11·11	2	16	10·39

Ann. der Chem. und Pharm., lxxxix. p. 214.

PROCEEDINGS OF SOCIETIES.

Royal Society.

March 2, 1854. (Professor Graham, V.P., in the Chair.) The following paper was read:—

"Note on the Decomposition of Sulphuric Acid by Pentachloride of Phosphorus." By Alexander Williamson, Ph.D., F.C.S., Professor of Practical Chemistry in University College.

Chemists have long been aware of the fact that some acids unite with bases in one proportion only, others in two or more proportions. Thus a given quantity of nitric acid forms with what is termed its equivalent of potash, a definite nitrate of potash; if less than this

equivalent quantity of potash were added to the nitric acid, the product would be a mechanical mixture of the same nitrate of potash with uncombined nitric acid; if more than the equivalent of potash were added, the excess of alkali would remain uncombined. Sulphuric acid, on the other hand, is capable of forming two compounds with potash, and it depends upon the proportions in which the two substances are brought together whether the neutral or acid sulphate is formed.

The number of compounds which an acid forms with one base is now considered as indicating its atomic weight. The weights of sulphuric and nitric acids which are respectively susceptible of neutralizing the same quantity of potash are termed *equivalent*, but these are by no means the same as their *atomic* weights. Sixty-three parts of nitric acid (nitrate of water) contains the same quantity of hydrogen as forty-five parts of sulphuric acid, and when they are neutralized by potash the whole of this hydrogen is removed and replaced by potassium; and if neither of the acids could combine in any other proportion with potash, their atomic weights would be the same as their equivalent weights. But sulphuric acid also forms a potash compound in which half of its hydrogen is replaced by potassium, the other half remaining in the compound, whereas the smallest particles of nitric acid either exchange the whole or none of their hydrogen for potassium.

This fact is expressed in the simplest possible manner by the statement that the smallest indivisible particles of sulphuric acid contain two atoms of hydrogen, whilst those of nitric acid only contain one. Thus it is, that whereas the equivalent weights of the two acids are the quantities which contain the same amount of basic hydrogen, their atomic weights must be in the proportion of two equivalents of sulphuric to one of nitric acid. The simplest expression for an atom of nitric acid being empirically NO^3H, we shall accordingly represent an atom of sulphuric acid by the formula SO^4H^2. In like manner, an atom of common phosphoric acid, being tribasic, is expressed empirically by the formula PO^4H^3. The labours of Messrs. Laurent and Gerhardt greatly contributed to the establishment of these results, which are uncontroverted.

We have hitherto been accustomed to resort very freely to imaginary distinctions of form and arrangement of matter to explain the differences of properties; but of late years an opposite tendency has arisen, and chemists have felt the necessity of reducing their language and ideas to simpler and more consistent forms. This necessity was first felt in the most complex, *i. e.* the so-called organic part of chemistry. But the simplifications thus introduced have proved to be equally applicable to the inorganic part of the science; and their introduction is calculated to disengage, for the consideration of substantial differences of composition, the attention which has hitherto been absorbed by imaginary distinctions of form. Being unable to express the constitution of compounds without some formal artifice, we shall be able to see and compare their substantial differences most easily when all unnecessary variations of those formal artifices

are eliminated. The success of this operation of course depends on our finding one form sufficiently general to replace the special and limited forms now employed.

In some papers published in the Journal of the Chemical Society two or three years ago, I endeavoured to show that the constitution of salts may be reduced to the type of water; that acids and bases being, truly, acid salts and basic salts, are perfectly conformable to the same principle; and that, amongst other things, the difference between monobasic and bibasic acids, &c. admits of a simple and easy explanation by it. The leading propositions in those papers have been adopted by several eminent chemists in this country and in France; and M. Gerhardt speedily enriched science with a series of brilliant and striking illustrations of their truth. As regards the constitution of bibasic acids, M. Gerhardt's results were, however, at variance with that theory; and he was led to represent them by formulæ equally inconsistent with his own previous views on the subject. I believe that this discrepancy is satisfactorily removed by the facts I have the honour of submitting to the consideration of the Society.

An atom of nitric acid, being eminently monobasic, is, as we have already shown, represented in the monobasic type $\overset{H}{H}O$ by the formula $\overset{(NO^2)}{H}O$, in which peroxide of nitrogen (NO^2) replaces one atom of hydrogen. In like manner, hydrate of potash $\left(\overset{H}{K}O\right)$ is obtained by replacing one atom of hydrogen in the type by its equivalent of potassium; and nitrate of potash $\left(\overset{NO^2}{K}O\right)$ by a simultaneous substitution of *one* atom of hydrogen by peroxide of nitrogen, the *other* by potassium. Sulphuric acid is formed from two atoms of water $\begin{matrix}H\\H\\H\end{matrix}\begin{matrix}O\\O\end{matrix}$; one of hydrogen from each is removed, and the two replaced by the indivisible radical SO^2. The series

Sulphuric acid.	Acid sulphate of potash.	Neutral sulphate of potash.
$\begin{matrix}H\\SO^2\\H\end{matrix}\begin{matrix}O\\\\O\end{matrix}$,	$\begin{matrix}H\\SO^2\\K\end{matrix}\begin{matrix}O\\\\O\end{matrix}$,	$\begin{matrix}K\\SO^2\\K\end{matrix}\begin{matrix}O\\\\O\end{matrix}$

explains itself.

Chemists have long known how to remove the basylous constituents H, K, &c. of these salts, and to replace them by others. But it is only recently that they have learnt to remove the chlorous radicals SO^2, NO^2, &c. in a similar manner. To obtain the chloride of potassium from its sulphate, it is sufficient to bring the latter into liquid contact with chloride of barium; but the same reagent would be powerless for the preparation of the chlorides of the radicals SO^2 or NO^2.

M. Cahours has shown us a reagent (the pentachloride of phosphorus) which is capable of forming from a great number of mono-

basic acids the chlorides of the acid radicals. Whilst extending our knowledge of the action of the body on monobasic and organic acids, and preparing numerous compounds of their radicals with one atom of chlorine, M. Gerhardt examined also the nature of its action upon bibasic acids and their compounds; and states that it consists of two successive phases, first, the liberation of the anhydrous acid, secondly, the substitution of two atoms of chlorine for one of oxygen in that anhydrous acid. These facts, if correct, would be unfavourable to the above view of the constitution of sulphuric and the other bibasic acids; and M. Gerhardt adopted accordingly the old formulæ, representing in their composition an atom of water ready-formed, SO^3H^2O.

Confining my remarks for the present to the case of sulphuric acid, whose decomposition is doubtless typical of that of other bibasic acids, I may state as the result of numerous experiments with the most varied proportions of pentachloride and acid, performed on a scale of considerable magnitude, that the first action of the pentachloride consists in removing one atom of hydrogen and one of oxygen (empirically peroxide of hydrogen) from the acid, putting in an atom of chlorine in their place and forming the compound $SO^2\begin{matrix}H\\Cl\end{matrix}O$, which is strictly intermediate between the hydrated acid and the final product SO^2Cl^2 formed by a repetition of the same process of substitution of chlorine for peroxide of hydrogen. The existence and formation of this body, which we may call chloro-hydrated sulphuric acid, furnishes the most direct evidence of the truth of the notion, that the bibasic character of sulphuric acid is owing to the fact of one atom of its radical SO^2 replacing or (to use the customary expression) being equivalent to two atoms of hydrogen. Had this radical been divisible like an equivalent quantity of a monobasic acid, we should have obtained a *mixture*, not a *compound* of the chloride with the hydrate,—or, at least, the products of decomposition of that mixture.

Chloro-hydrated sulphuric acid boils at 145° Cent., distilling without decomposition. The intensity of its action upon water varies according to the manner in which the two bodies are brought together. When poured rapidly into a large quantity of cold water, a portion of it sinks to the bottom, and only gradually dissolves as a mixture of hydrochloric and sulphuric acids. When a small quantity of water is added to the compound, the same decomposition takes place with explosive violence. The acid dissolves chloride of sodium on the application of a gentle heat with evolution of hydrochloric acid, giving rise to a compound of the formula $SO^2\begin{matrix}Na\\Cl\end{matrix}O$. When poured upon pieces of melted nitre at the atmospheric temperature, an effervescence takes place with evolution of a colourless vapour which possesses in a striking degree the odour of aqua regia. This vapour may be dissolved in various liquids, and when decomposed by water, yields nitric and hydrochloric acids. It is doubtless

chloro-nitric acid, NO^2Cl. In like manner the chlorides of other inorganic acid radicals may be obtained, as from chlorates, perchlorates, sulphites, &c., but of these and other reactions I beg leave to defer any further account until the experiments now in hand are more advanced.

From the general resemblance of properties and identity of boiling-point of the chloro-hydrate with a compound discovered by Rose, and described by that eminent chemist as possessing empirically the composition $S^2O^5Cl^2$, I was led to suspect that the two might in reality be identical, which of course would require the addition of the elements of water to Rose's formula, and several experiments I have performed afford strong confirmation of that identity. The same compound is obtained by the action of dry hydrochloric acid on anhydrous sulphuric acid; and finally, I may mention that Mr. Railton obtained a small quantity of the same substance some weeks ago in my laboratory by the action of platinum-black at a high temperature on an imperfectly dried mixture of chlorine and sulphurous acid.

As regards the successive transformations effected in the pentachloride, I have observed the formation of Wurtz's oxychloride (the tribasic chloro-phosphoric acid ($PO\,Cl^3$)), and also of a compound boiling above 145°, probably PO^2Cl. Hydrated phosphoric acid is always formed unless the amount of pentachloride added is very great.

March 16. (Charles Wheatstone, Esq., V.P., in the Chair.) The following paper was read:—

"On some new Compounds of Phenyle." By A. Williamson, Ph.D., F.C.S., Professor of Practical Chemistry in University College.

This communication contains a notice of some of the results obtained in an investigation of Carbolic Acid or Hydrated Oxide of Phenyle, conducted, under the author's superintendence, by Mr. Scrugham in the Analytical Laboratory of University College.

Referring to the substitution products obtained by Laurent from hydrate of phenyle by the action of chlorine and bromine, as well as to its combination with acids prepared by that chemist in conjunction with Gerhardt, the author states that the substance which they conceived to be chloride of phenyle has been found by Mr. Scrugham to be a mixture of two compounds.

As regards the preparation of hydrate of phenyle from the creosote of coal-tar, it is observed that the numerous fractional distillations by which it is usually isolated may be abridged by crystallization; for if creosote, having the boiling-point between 186° and 188° Cent., be left for some time in contact with a few crystals of the pure hydrate, it deposits a considerable quantity of beautiful colourless needles, which, when separated from the mother-liquid, distil at 184° Cent., and condense in the neck of the retort into a solid mass of pure hydrate of phenyle.

When pentachloride of phosphorus is added to hydrate of phenyle, the action is at first very energetic, hydrochloric acid being evolved,

and the mixture becoming hot; but after a time the addition of fresh portions of pentachloride produces no perceptible action, unless the mixture be heated. Oxychloride of phosphorus is formed, as well as a neutral oily body, which is insoluble in aqueous potash at the common temperature, but soluble with decomposition in boiling potash. This oily compound would, from its mode of formation, be naturally supposed to be the chloride of phenyle, and it has been so considered by some distinguished chemists. It may, however, be separated by distillation into two perfectly definite and distinct bodies, one of which boils at 136° Cent., the other at a temperature above the range of mercurial thermometers. The former of these is a colourless mobile liquid, possessing a fragrant smell, not unlike that of bitter almonds. The latter is a more consistent inodorous liquid, which solidifies at a low temperature into a mass of colourless crystals. The liquid having the boiling-point of 136° is nothing else than the *chloride of phenyle*. The crystalline body is the *phosphate of phenyle*, one of the most beautiful products in organic chemistry. In the liquid state it is slightly yellow by transmitted light, and it reflects the more refrangible rays with a fine opalescent appearance, due no doubt to the so-called epipolic refraction. The epipolic rays visible by ordinary daylight on and at some depth below its surface, are of a fine violet tint, differing decidedly from the blue colour exhibited by disulphate of quinine in like circumstances. The flame of sulphur does not bring out this effect more strongly than the diffused light of the sun.

Phosphate of phenyle dissolves in strong nitric acid with evolution of considerable heat, and the solution gives out nitrous fumes on ebullition. A heavy yellow oil is precipitated by water from this solution, and collects in drops which ultimately solidify, and their solidification is, singularly enough, accelerated by *hot* water, by reason of its more quickly dissolving out the nitric acid which at first holds the solid body in solution. *Nitrophosphate of phenyle* is an acid, and forms with potash a beautiful crystalline salt.

An alcoholic solution of phosphate of phenyle decomposes acetate of potash on ebullition. After the alcohol is distilled off, the temperature of the mixture rises rapidly on the application of further heat, and a limpid oleaginous substance, having a very peculiar odour, distils over, which possesses the composition of *acetate of phenyle*. This compound boils at 190° Cent.; it is heavier than water, and very slightly soluble in that liquid. It dissolves with decomposition in boiling potash.

Cyanide of phenyle is obtained by the action of the phosphate on cyanide of potassium. It is decomposed by boiling potash with evolution of ammonia.

Terchloride of phosphorus, when distilled with hydrate of phenyle, seems to act at first similarly to the pentachloride, but the phosphite of phenyle formed is decomposed by heat; and among the products of distillation is found a body boiling at 80° Cent., and possessing all the properties of *benzine*, i. e. *hydruret of phenyle*.

The formation of the *iodide of phenyle* is necessarily attended with

some difficulty, owing to the circumstance of phosphorus not combining with more than three equivalents of iodine. Its boiling-point is 190° Cent.

Mr. Scrugham has had reason to confirm the statements of Laurent and Gerhardt respecting the *benzoate of phenyle*, and has prepared that compound in considerable quantities by the action of chloride of benzoyle on phenylate of potash. Chloride and phosphate of phenyle could not be made to react on benzoate of potash.

Chloride of cuminyle reacts with violence on phenylate of potash, with formation of *cuminate of phenyle*, a compound analogous to the benzoate.

Chloride of phenyle was heated with phenylate of sodium, with a view to the formation of *oxide of phenyle*, and there is no doubt that this compound was formed by the reaction, as the correlative product, chloride of sodium, was detected. But a further account of this and other reactions is deferred until the experimental investigation is more advanced.

Specimens of most of the compounds mentioned were exhibited.

March 30. (Thomas Bell, Esq., V.P., in the Chair.) The following paper was read:—

"Note on the Melting-point and Transformations of Sulphur." By B. C. Brodie, Esq., F.R.S.

In the treatises of chemistry where the results of different observers are collected, various statements will be found as to the melting-point of sulphur. The numbers given in Gmelin's Chemistry vary from 104°·5 C. to 112°·2 C., but of five chemists cited, no two agree as to this apparently simple fact. There is evidently some peculiarity about this melting-point which is the cause of these anomalous results. In some experiments on allotropic substances, in which I have been engaged, I had occasion to submit this question to a more searching inquiry than it had hitherto received, in which I have discovered the cause of these discrepancies. In the present note I will briefly give the results at which I have arrived, reserving the details for a further and more full communication.

The melting-point of sulphur varies according to its allotropic condition. This condition is readily altered by heat, and invariably, without peculiar precautions, by melting. Hence the temperature at which sulphur melts is different from that at which it will solidify, or at which, having been melted, it will melt again.

The melting-point of the octohedral sulphur, as crystallized from the bisulphide of carbon, is 114°·5 C. But from the facility with which this sulphur, when heated even below its melting-point, passes into the sulphur of the oblique system, this fact may readily be overlooked. When this sulphur, in the state of fine powder, is heated even for the shortest time between 100° and 114°·5, this change cannot be avoided. For the transformation of large crystals a longer time is required. At a certain point the crystal becomes opake, and is often broken in pieces at the moment of the change. When in such a crystal this change has either entirely or par-

tially taken place, the melting-point will be above 114°·5. The minute crystals of sulphur from alcohol, which are so extremely thin that their angles cannot be measured, have this melting-point of 114°·5, which fixes the system to which the crystals belong. The crystals of sulphur from benzole (rectified coal naphtha) melt also at 114°·5. The crystals from alcohol are very minute, consequently so readily transformed, that they presented anomalies which led me to doubt whether sulphur of both forms did not exist among them. I answered this question by dividing a certain number of carefully selected crystals, and taking the melting-point of the two halves of the same crystal. I found that these melting-points in many cases did not correspond, which would have been the case if the anomalies had arisen from the different nature of the crystals. Sulphur which has been melted at 114°·5, and of which the temperature has not been raised above 115°, remains, on solidification, perfectly transparent for any length of time. Heated beyond this point, it becomes, on cooling, more or less opake.

When sulphur has been converted by heating for a sufficient length of time, in the manner above mentioned, between 100° and 114°·5, it acquires a fixed melting-point of 120° C. This is the melting-point of the oblique prismatic sulphur. If sulphur thus converted be carefully melted so as to raise the temperature as little as possible above the melting-point, no sensible difference will be observed between the point of melting and of solidification. To obtain this fixed melting-point of 120°, care must be taken that the transformation of the sulphur has been thoroughly effected. If this be not done, it may melt at any point between 114°·5 and 120°. If, however, the temperature of the melted sulphur be raised above its melting-point of 120°, the point of solidification will be altered, and may lie even below the first melting-point of 114°·5*. The point of solidification is in this case not fixed, but depends upon the temperature to which the sulphur is raised and upon the mode in which it is cooled. It has varied in my experiments from 118° to as low as 111°. When the melting-point of the sulphur, thus solidified, is taken, it will begin to melt at about the temperature of solidification. The cause of this anomaly is evident. When the temperature of sulphur is raised above 120°, a transformation into the viscid form instantly commences, so that the sulphur is a mixture of the two varieties, and the melting-point varies according to the proportion in which these two varieties are mixed. It varies inversely with the temperature to which the sulphur is raised, so that the presence of the viscid sulphur lowers the point of solidification. There is, however, a limit beyond which the melting-point is not affected by this admixture. I made the experiment of pouring sulphur, heated to its boiling-point, into water of different temperatures, and of taking the melting-point of the sulphur when it had become hard. Five different preparations,

* This has been observed by Person, who states that if sulphur be heated above 150° its melting-point is lowered to about 112° or 110°. He says, that when heated with care, the thermometer will remain constant during crystallization, at 115°. I have not found this correct.—Ann. de Chemie, vol. xxi. p. 323.

which, when extracted with bisulphide of carbon, gave each a different quantity of insoluble sulphur, coincided in the melting-point of about 112°. This sulphur, before melting, becomes transparent, and passes again into the viscid or elastic condition.

The sulphur which is insoluble in bisulphide of carbon, and which is prepared by extracting the hardened viscid sulphur with that reagent, has a melting-point considerably above 120°, but which I have not been able to determine with precision.

I had placed in a water-bath, at 100°, tubes containing fragments of the three definite varieties of sulphur. After a short time, on examining the tubes, I found the insoluble sulphur, which I have stated to have such a high melting-point, distinctly melted. The octohedral sulphur had become opake and rounded at the edges, the other was unaltered in appearance. Further inquiry convinced me that the cause of the melting of the insoluble sulphur was, that it had passed into another modification, and that this conversion was attended with evolution of heat sufficient to melt the sulphur. The insoluble sulphur thus converted remains transparent, and is perfectly soluble in bisulphide of carbon.

It is stated in chemical treatises that the opacity which on solidification comes over the melted sulphur, is due to the transformation of the oblique prismatic into the octohedral sulphur, and the consequent disruption of the crystal. To this cause also is attributed the evolution of heat which has been observed in solid sulphur immediately after cooling. There are, however, no sufficient grounds for this view, and some of the observations which I have given are decidedly adverse to it. 1. The change readily takes place, even at temperatures at which sulphur becomes opake, in the opposite direction, namely, from the octohedron to the oblique prism. 2. The melting-point of the opake sulphur coincides too nearly with its point of solidification for it to be supposed that this change in it has taken place. On extracting melted sulphur which had become opake, with bisulphide of carbon, I have constantly found present traces of insoluble matter, even where the greatest precaution had been taken to avoid elevation of temperature; and this opacity appears to me to be due to the hardening of the viscid sulphur, and the consequent deposition of opake matter in the pores of the crystals, which is quite sufficient to account for it. It remains to ascertain the cause of the evolution of the heat. On this point also I will offer a suggestion. It is well known that the appearance of opacity is delayed by pouring the sulphur into cold water, and that the sulphur thus formed is at first viscid and transparent, and only after a time becomes solid and opake. The received view, I believe, is that the hard sulphur thus formed is the solid form of the viscid sulphur, in the same sense as ice is the solid form of water. It appears to me more probable that these two sulphurs stand in a different relation, and that the change which takes place on solidification is an allotropic transformation of the viscid sulphur into the insoluble sulphur and one of the other modifications. In the case of sulphur gradually cooled this change takes place with rapidity, and, like other similar transformations, is attended

with a sensible evolution of heat. Where the sulphur is *tempered* the change takes place very slowly, and the heat evolved is not perceived. This view is confirmed by a fact which I have discovered, namely, that the viscid sulphur possesses another solid form. I have found that when sulphur, melted at a high temperature, is suddenly exposed to intense cold—the cold of solid carbonic acid and æther—the sulphur formed is not viscid, but solid, hard, and perfectly transparent. When the temperature is allowed to rise to that of the air, the sulphur becomes soft and elastic. It is probable that this is the true solid form of the viscid sulphur.

April 6. (Thomas Graham, Esq., V.P., in the Chair.) The following paper was read :—

"On a new Series of Sulphuretted Acids." By Dr. August Kekulé. Communicated by Dr. Sharpey, Sec. R.S.

Adopting the idea that the series of organic compounds of which sulphuretted hydrogen is the type, corresponds in every respect with the series of which water is the type, I concluded that not only mercaptans and neutral sulphides which correspond to the alcohols and æthers, but also compounds corresponding to the acids, anhydrous acids and æthers of acids might be produced; I therefore endeavoured to obtain reactions which would enable me to replace oxygen in the compounds of the latter series by sulphur.

Such reactions are produced by the compounds of sulphur with phosphorus—the tersulphide ($P^2 S^3$) and the pentasulphide ($P^2 S^5$)—which are easily obtained by fusing together amorphous phosphorus and sulphur in an atmosphere of carbonic acid; no explosion takes place, although the combination is attended with a very violent action.

Experiment has proved that these combinations of sulphur and phosphorus act on the members of the series of water in the same manner (although less violently) as the corresponding compounds of chlorine and phosphorus;—however, with this difference, that by using the chlorine compounds the product is resolved into *two* groups of atoms, while by using the sulphur compounds there is obtained only *one* group; a peculiarity, which, according to the bibasic nature of sulphur, must have been expected. By acting on these compounds of sulphur and phosphorus with water one atom of sulphuretted hydrogen is obtained, while the chlorides give two atoms of hydrochloric acid,

$$6\left.\begin{matrix}H\\H\end{matrix}\right\} O + P^2 S = 3\left.\begin{matrix}H\\H\end{matrix}\right\} S + 2PO^3 H^3$$

$$6\left.\begin{matrix}H\\H\end{matrix}\right\} O + 2P Cl^3 = 6H Cl + 2PO^3 H^3.$$

Similar reactions are observed with organic compounds belonging to the series of water with the formation of phosphorous and phosphoric acids respectively, or a conjugate acid. By acting in this way, the following series of sulphuretted organic compounds is obtained, by the side of which are placed for comparison the products

formed by the action of the chlorides of phosphorus on the same substances.

Sulphuretted Hydrogen.
$$\left.\begin{matrix}H\\H\end{matrix}\right\}S.$$
Hydrochloric Acid.
$$2HCl.$$

Mercaptan.
$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}S.$$
Chloride of Æthyle + Hydrochloric Acid.
$$C^2H^5Cl + HCl.$$

Sulphide of Æthyle.
$$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}S.$$
Chloride of Æthyle.
$$2C^2H^5Cl.$$

Othyl-Hydrosulphuric Acid.
$$\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}S.$$
Chloride of Othyle + Hydrochloric Acid.
$$C^2H^3O,Cl + HCl.$$

Othyl-Sulphide of Othyle.
$$\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}S.$$
Chloride of Othyle.
$$2C^2H^3O,Cl.$$

Othyl-Sulphide of Æthyle.
$$\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}S.$$
Chloride of Othyle + Chloride of Æthyle.
$$C^2H^3O,Cl + C^2H^5Cl.$$

Mercaptan is obtained by the action of tersulphide or pentasulphide of phosphorus on alcohol with extreme facility. Sulphide of æthyle may also be prepared by acting on æther in a similar manner.

Thiacetic Acid,—Sulphuretted Acetic Acid,—has been obtained by me by acting on monohydrated acetic acid with tersulphide of phosphorus. It is a colourless liquid, boiling at about 93° C., and has a peculiar odour resembling sulphuretted hydrogen and acetic acid. It dissolves potassium in the cold and zinc on heating with the evolution of hydrogen, and gives with lead a salt less soluble than the ordinary acetate, so that it gives a precipitate with acetate of lead. By recrystallization from water or alcohol, the lead salt is obtained in fine silky needles, which, though quite colourless at first, are rapidly decomposed (whether in solution or in the solid form) with the formation of sulphuret of lead.

By analysis I found the lead salt contained—

Lead 58·8 per cent. Theory requires 58·0 per cent.

The acid contained—

Sulphur 41·3 per cent. Theory requires 42·1 per cent.

Thiacetic acid is also formed in small quantity and by secondary action, by distilling pentasulphide of phosphorus with fused acetate of soda. Pentachloride of phosphorus gives a violent reaction with thiacetic acid, yielding sulphochloride of phosphorus, chloride of othyle, and hydrochloric acid,

$$\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}S + PCl^5 = C^2H^3OCl + HCl + PSCl^3.$$

Thiacetate of Othyle.—Sulphide of Othyle.—Anhydrous Sulphuretted Acetic Acid.—Pentasulphide of phosphorus acts but very feebly upon

anhydrous acetic acid in the cold, but on heating a violent reaction takes place. By distilling the product, the anhydrous acid is obtained in the form of a colourless liquid, boiling at about 121° C., and having an odour greatly resembling sulphuretted acetic acid. On mixing with water it falls to the bottom, without, at first, suffering any change; on standing, however, it is slowly dissolved and decomposed into sulphuretted acetic acid and ordinary acetic acid. This change takes place much more rapidly on heating,

$$\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}S+\left.\begin{matrix}H\\H\end{matrix}\right\}O=\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}S+\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O.$$

It appears that anhydrous sulphuretted acetic acid is also produced by acting on the othyle-sulphide of lead with chloride of othyle, at all events chloride of lead is formed. Chloride of benzoyle gives with the lead salt a similar reaction, and it is probable that an intermediate sulphuretted acid is formed, having the formula

$$\left.\begin{matrix}C^2H^3O\\C^7H^5O\end{matrix}\right\}S.$$

Thiacetate of Æthyle.—Sulphuretted Acetic Æther.—This compound may be prepared by the action of pentasulphide of phosphorus on acetic æther. It is a liquid lighter than water, and possesses an odour resembling acetic æther and sulphuretted hydrogen. It boils at about 80° C.

It will be seen that the action of tersulphide and pentasulphide of phosphorus above described produces sulphuretted organic compounds by substituting sulphur for oxygen. The compounds obtained in this way may also be formed by replacing one or two atoms of hydrogen in sulphuretted hydrogen (H^2S), or one or two atoms of metal in sulphide of potassium (K^2S), or in sulphide of hydrogen and potassium (KHS), by organic radicals. Mercaptan, and the sulphides of alcohol radicals have, in fact, been long obtained in this manner.

The formation of a sulphuretted compound containing an acid radical has been observed by Gerhardt by acting on sulphide of lead with chloride of othyle. I have not made many experiments of this kind, but I have observed that chloride of benzoyle is not decomposed by sulphuretted hydrogen, while it (as well as chloride of othyle) gives a reaction with sulphide of hydrogen and potassium yielding chloride of potassium.

I am continuing these researches, and believe the above reactions will furnish many new compounds, and will tend to complete our knowledge of some of those organic and inorganic compounds now known.

THE CHEMICAL GAZETTE.

No. CCLXXIX.—June 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Examination of some Products of the Transformation of Creatine. *By* M. Dessaignes.

Oxide of mercury, when heated with an aqueous solution of creatine or of creatinine, acts upon both these bodies. The fluid evolves an odour which is peculiar to the products of the dry distillation of creatine, and which has been compared by M. Chevreul to that of phosphorus. Carbonic acid is disengaged without any trace of ammonia, and the oxide of mercury is partially reduced. The principal product of the reaction consists in a crystalline body, which I declared, some time since, to be a new alkaloid, on account of its alkaline reaction. I have resumed the investigation of this subject; the crystals obtained with creatinine are not homogeneous. By the employment of alcohol and repeated crystallizations, I at last obtained,—1st, crystals which were sparingly soluble in water, and still more sparingly in alcohol, neutral to test-papers, efflorescent at 212° F., and recognizable as creatine by all their characters; 2nd, a larger quantity of flattened prisms, attached to one another by their sides and imbricated. Creatine, when the oxide of mercury was present in sufficient excess, produced only these latter crystals.

This substance is very soluble in water; it has a disagreeable taste, and becomes opake at 212° F., losing water. When heated on platinum foil, it emits the same odour as creatine; it imparts a slight blue colour to reddened litmus-paper. Brought into contact with potash in the cold, it evolves no ammoniacal odour; it precipitates the chlorides of barium and calcium, nitrate of silver and acetate of lead. This last precipitate, when washed and decomposed by sulphuretted hydrogen, furnished oxalic acid. That which I took for an alkaloid is consequently the oxalate of a strong base. This base was isolated by heating its oxalate with a very small excess of pure milk of lime and filtering. By evaporating *in vacuo*, I obtained a colourless body, with a crystalline surface, which is perhaps to be attributed to the absorption of carbonic acid by this alkali, as it attracts it strongly. It is also deliquescent; it has a very caustic and somewhat ammoniacal taste. When heated on platinum foil, it is almost entirely volatilized, with a strong odour of burnt creatine; it expels ammonia from its salts in the cold, and produces copious precipitates with chlorides of barium and calcium. The pre-

cipitates are soluble in a large quantity of water, and also in weak acetic acid, without effervescence. It precipitates sulphate of alumina and chloride of iron, the precipitates dissolving in an excess of the precipitant. It produces a white precipitate with a yellowish tinge with nitrate of silver; it dissolves oxide and chloride of silver. It also precipitates the salts of mercury, lead and copper.

With the oxalate of this alkali and chloride of calcium, or nitrate and sulphate of lime, crystallized salts may be readily prepared; they have a weak alkaline reaction. With its hydrochlorate and chloride of platinum in concentrated solutions, superb orange rhombohedral crystals are obtained after some time; these consist of a double salt, which, when redissolved and crystallized by cooling, often takes the form of flat prisms, attached side by side; the coloured mother-liquors, obtained in the preparation of the oxalate, have a strongly alkaline reaction upon paper. When deprived of oxalic acid by chloride of calcium, they furnish with chloride of platinum a considerable quantity of the double salt which has just been mentioned.

The oxalate prepared from creatine lost 13·25 per cent. of water at 212° F.; the same salt furnished a quantity of oxalate of lime, which, when dried at 212° F., represented 38·41 per cent. of $C^2 H^2 O^4$. By combustion with oxide of copper and oxygen, and with soda lime for the nitrogen, I found that the same salt, dried at 212° F., contained—

	Found.		Calculated.
Carbon	30·90	4	30·50
Hydrogen	6·93	14	6·77
Nitrogen	35·05	6	35·59

The oxalate produced from creatinine lost 13·34 per cent. of water at 212° F. Dried at this temperature, it contained in 100 parts—

Carbon	30·98
Hydrogen	7·27
Nitrogen	35·43

The hydrated oxalate, according to the formula $C^4 H^{14} N^6$, $C^2 H^2 O^4$, $H^4 O^2$, ought to lose 13·23 per cent. of water at 212° F., and contains 38·14 per cent. of monohydrated oxalic acid.

I also analysed the platino-chloride dried *in vacuo*:—

	Found.		Calculated.
Carbon	8·77	4	8·60
Hydrogen	3·03	16	2·87
Nitrogen	14·85	6	15·05
Chlorine	38·71	6	38·18
Platinum	35·19	1	35·30

The composition of this remarkable base is therefore represented by the formula $C^4 H^{14} N^6$. What is its constitution? Just as creatine may be represented as urea and sarcosine conjoined, with elimination of water, this new base appears to be a conjugate compound of urea and methylamine with elimination of water. Thus—

$$C^4 H^{14} N^6 + H^4 O^2 = C^2 H^8 N^4 O^2 + C^2 H^{10} N^2.$$

This base, which may be called *methyluramine*, when heated with a solution of baryta, is decomposed, ammonia being evolved accompanied by a fishy odour. The platino-chloride, when heated, emits an odour of trimethylamine. Sarcosine may be represented as glycollate of methylamine *minus* water, and it no doubt bears the same relation to glycollic methylamine that sugar of gelatine does to glycollamide. It is the elements of glycollic acid in the creatine which are oxidized by the oxide of mercury so as to produce oxalic acid, carbonic acid and water, as expressed in the equation

$$C^8 H^{18} N^6 O^4 + O^5 = C^4 H^{14} N^6, C^2 H^2 O^4 + C^2 O^4 + H^2 O.$$

I have also attempted to throw some light upon the constitution of creatine, by submitting it to the action of nitrous acid, and this inquiry has enabled me to recognize a character of this interesting body which had escaped M. Liebig. Creatine differs, it is true, from sugar of gelatine, and other analogous bodies, by its refusing to combine with metallic oxides; but it resembles them in combining with acids to form beautiful crystalline compounds with a strongly acid reaction. If a rapid current of nitrous acid gas be passed into water containing an excess of undissolved creatine, the latter is quickly dissolved, and a large quantity of small brilliant crystals afterwards make their appearance. These crystals, which may readily be obtained in thick short prisms by solution in warm water and cooling, consist of nitrate of creatine. Their solution, which has a very acid taste, is abundantly precipitated by ammonia. The precipitate, dissolved in hot water, furnishes on cooling small prisms, which effloresce at 212° F., and the solution of which is neutral with paper, and does not produce precipitates with chloride of mercury, chloride of zinc or nitrate of silver. These prisms, dried at 212° F. and analysed, furnished in 100 parts—

	Found.	Calculated (anhydrous creatine).
Carbon	36·77	36·64
Hydrogen	7·13	6·87
Nitrogen.....	32·18	32·06

I also determined the quantity of nitric acid in the nitrate of creatine, and found it to contain 32·36 per cent. of monohydrated nitric acid. The formula $C^8 H^{18} N^6 O^4, N^2 H^2 O^6$ requires 32·47 per cent. of $N^2 H^2 O^6$. The same compound was produced by dissolving 1·057 gr. of crystallized creatine in nitric acid containing 0·447 gr. of $N^2 H^2 O^6$, and evaporating at 86° F. The crystals were homogeneous, and weighed 1·373 gr. From calculation they should weigh 1·376 gr. The sulphate and muriate of creatine form fine prisms, which are more soluble than the nitrate, but like this are not deliquescent; they may be obtained by direct combination with the acids, and evaporating at 86° F. or *in vacuo*. From these I have separated the creatine free from all traces of creatinine; I have also determined their proportions by synthesis, and their formulæ are $C^4 H^{18} N^6 O^4, SH^2 O^4$ and $C^4 H^{18} N^6 O^4, Cl^2 H^2$. The solution of nitrate of creatine, traversed by a current of nitrous vapour, disen-

gages much gas; but the reaction, however long it might be continued, did not give rise to an acid free from nitrogen. By neutralizing the product with potash, separating the greater part of the nitrate of potash by crystallization, and then adding nitrate of silver, crystals soluble in hot water are obtained, which after several crystallizations acquire the form of long white needles, which become slightly yellow when exposed to the light. This salt is a compound of nitrate of silver and of a new alkaloid. When calcined, it evolves a fishy odour; it contains in 100 parts—

Carbon	16·29
Hydrogen	2·37
Silver	47·97

which may be represented by the formula $C^6 H^{10} N^2$, $N^2 AgO^6$. This salt, decomposed by the exact quantity of muriatic acid, furnished the chloride of the alkaloid which it contains. This chloride crystallizes in a fibrous mass or in little prisms; it is very acid to the taste. With bichloride of mercury it produces long needles of a double salt, from which the organic base may be isolated; but before I can pursue the investigation of this base, I must prepare a fresh supplyof creatine.—*Comptes Rendus*, May 8, 1854, p. 839.

On Glucinum and its Compounds. *By* H. Debray.

M. Wöhler obtained the metal of glucina by means of the reducing action of potassium upon the chloride of glucinum; he assigns to it the following properties:—

"Glucinum forms a dark gray powder, having exactly the appearance of a metal precipitated in a very divided form. Under the burnisher it acquires a dull metallic lustre. As it is not agglomerated by the violent heat at which it is reduced, it may be imagined that it is very difficult of fusion. It does not oxidize in the air at ordinary temperatures, nor in water even when boiling. Heated on platinum foil in contact with the air, it takes fire, and burns with a brilliant flame, becoming converted into white glucina.

"It dissolves readily in sulphuric, muriatic and nitric acids; in the two former with disengagement of hydrogen, in the latter of nitrous acid gas."

The recent researches upon aluminium have induced me to take up the study of glucinum; assisted by the advice of M. Sainte-Claire Deville, and by availing myself of his methods, I have been enabled to obtain some new results, which I think worthy of the notice of the Academy.

Glucinum is the lightest of all the known metals which do not decompose water at ordinary temperatures or at the boiling-point; its density is 2·1. It is therefore lighter than aluminium. From its appearance it might be confounded with zinc; but its less degree of fusibility, which places it between the latter metal and aluminium, its fixity in the fire, and its low specific gravity are so many physical properties which would suffice to distinguish it from zinc.

Although unalterable at ordinary temperatures, it becomes oxidized on the surface at the highest temperature produced by the blowpipe, but without ever presenting the phænomenon of ignition, which is produced when zinc or iron are placed in similar circumstances. Concentrated nitric acid only acts upon it when hot. Weak nitric acid does not dissolve it under any circumstances. Muriatic and sulphuric acids, even when diluted, dissolve it with evolution of hydrogen. Concentrated solution of potash dissolves it even when cold, but ammonia does not act upon it.

Glucina, from which a true metal is thus obtained, also furnishes well-crystallized salts, which I have carefully examined, and my researches on which will form a complete memoir, to be brought before the Academy very shortly.—*Comptes Rendus*, April 24, 1854, p. 784.

On the Composition of the Alkaloids of Harmala.
By J. Fritzsche.

The author has repeated the analyses of *harmaline*, *harmine* and *nitroharmalidine*. He has found that the formulæ of all these bodies contain 1 atom less carbon than was expressed by the formulæ formerly given by him.

He first describes the mode of combustion which he adopted in these analyses. It was performed by means of Hess's apparatus, but was not carried on from the commencement in a current of oxygen, but at first only at the expense of the oxygen of the oxide of copper. For this purpose, a narrow tube, 3 or 4 inches in length, was attached to the hinder end of the combustion-tube, and this was drawn out in the middle so as to enable it afterwards to be readily removed and closed up by fusion in the spirit-lamp; the tube thus prepared, which was 22 inches in length, and contained from 128 to 140 grms. of a granular oxide of copper, which had already been repeatedly employed, was filled in exactly the usual manner, that is to say, first a plug of copper turnings, then a little oxide of copper, then the mixture of the substance with oxide of copper, which is to be made in a porcelain mortar, and upon this a mass of oxide of copper of 4 inches in length, with another plug of copper turnings. After a passage for air had been produced in the tube by horizontal tapping, it was surrounded with sand at a temperature of 248°–266° F., and a stream of dry atmospheric air was passed through it from a gas-holder connected with the hinder end until any moisture which might have been contracted during the filling was completely got rid of. The combustion-tube was then sealed up at the part which had been drawn out by the flame of a spirit-lamp; the sand was removed, and the chloride of calcium tube and potash apparatus, as well as another tube beyond this containing dry caustic potash, attached to the combustion-tube. The union of the chloride of calcium-tube with the combustion-tube was effected by a carefully- and very tight-fitting cork, into which the chloride of calcium-tube was fastened with sealing-wax for greater

security. In order to prevent all loss of water through the cork, it was completely enclosed in a case carefully constructed of several pieces of cork held together by a caoutchouc band, and this was protected as much as possible from the action of heat by a pasteboard screen. The sealed end of the combustion-tube was now marked with a file without breaking it off, and whilst thus closed was united by a caoutchouc tube with a gas-holder containing oxygen gas; the combustion was then commenced at the expense of the oxide of copper. When the tube was at a red heat throughout its whole length, and only a very inconsiderable evolution of gas was taking place, the filed end of the combustion-tube within the caoutchouc tube was broken off, and the passage of oxygen gas through the tube commenced. The analysis was only considered as complete when all the reduced copper had again become completely oxidized, and oxygen had been passing out of the potash tube for some time.

In this manner the author has made two analyses of each of the alkaloids. *Harmaline* gave—

Carbon	72·90	72·83	26 =	1953·12	72·93
Hydrogen ..	6·51	6·43	28	174·72	6·52
Nitrogen	..	..	4	350·12	13·08
Oxygen.....	..	..	2	200·00	7·47

Muriate of harmaline consists of—

	Calculated.	Formerly found.
Harmaline	85·46	
Muriatic acid	14·54	14·124

and the per-centage quantities of each individual element are—

	Calculated.	Formerly found.
Carbon	62·33	63·130
Hydrogen.....	5·97	5·825
Nitrogen	11·17	
Oxygen.....	6·38	
Chlorine	14·15	

For the *muriate of harmaline*, containing 4 atoms of water of crystallization, the atomic weight 3583·64 is obtained, and it contains in 100 parts—

	Calculated.	Formerly found.
Muriate of harmaline.....	87·45	
Water.....	12·55	12·60

The atomic weight obtained for the *platinum double salt* is 5252·36; its per-centage composition is—

	Calculated.	Formerly found.
Carbon.....	37·18	37·625
Hydrogen.....	3·56	3·545
Nitrogen	6·67	
Oxygen.....	3·81	
Chlorine	25·32	
Platinum	23·46	23·275

The comparison of the numbers formerly ascertained for these compounds with those calculated from the new formula shows so close an agreement, that the author has considered it superfluous to repeat the analyses of these bodies.

The new analyses of *harmine* gave numbers agreeing with the formula $C^{26}H^{24}N^4O^2$:—

Carbon	73·73	73·78	26 =	1953·12	73·62
Hydrogen	5·62	5·64	24	149·76	5·64
Nitrogen	..	..	4	350·12	13·20
Oxygen.....	..	..	2	200·00	7·54

The atomic weight of *muriate of harmine* according to these numbers is 3108·76, and it consists of—

	Calculated.	Formerly found.	Per-centage elementary composition.	
Harmine.....	85·34		C....	62·82
Muriatic acid..	14·66	14·275	H ..	5·22
			N....	11·26
			O....	6·44
			Cl ..	14·26

The atomic weight obtained for *muriate of harmine*, containing 4 atoms of water of crystallization, is 3558·68, and it contains in 100 parts—

	Calculated.	Formerly found.
Muriate of harmine	87·36	
Water.....	12·64	12·43

For the *platinum double salt* we get the atomic weight 5227·40, and for its composition—

	Calculated.	Formerly found.
Carbon	37·36	37·90
Hydrogen	3·10	3·17
Nitrogen.....	6·70	
Oxygen	3·83	
Chlorine.....	25·44	
Platinum	23·57	23·25

The atomic weight obtained for *neutral sulphate of harmine* is 3266·23, and it consists of—

	Calculated.	Formerly found.
Harmine.....	81·23	
Sulphuric acid	15·33	15·14
Constitutional water	3·44	

Neutral sulphate of harmine, containing 2 atoms of water of crystallization, has the atomic weight 3491·19, and consists of—

	Calculated.	Formerly found.
Sulphate of harmine	93·56	
Water of crystallization....	6·44	6·57

The atomic weight of *acid sulphate of harmine* is 3879·46, and it consists of—

	Calculated.	Formerly found.
Harmine	68·39	
Sulphuric acid	25·81	25·59
Water	5·80	

These numbers, when compared with those formerly obtained for these compounds, agree so closely as to render new analyses superfluous.

It appears from the foregoing analyses that the atomic weight of *hydrocyanharmaline* must be 3015·24, and that it consists of—

	Calculated.	Formerly found.
Carbon	69·74	69·89
Hydrogen	6·21	6·49
Nitrogen	17·42	
Oxygen	6·63	

or—

	Calculated.	Formerly found.
Harmaline	88·80	89·04
Hydrocyanic acid	11·20	10·96

The atomic weight of *muriate of hydrocyanharmaline* will be 3471·50, and it contains—

	Calculated.	Formerly found.
Harmaline	77·14	
Hydrocyanic acid	9·73	9·51
Muriatic acid	13·13	12·86

Nitroharmalidine, in the new analyses, gave numbers agreeing with the formula $C^{26}\ H^{26}\ N^{6}\ O^{6}$:—

Carbon	60·13	60·31	26 =	1953·12	60·27
Hydrogen	4·94	4·91	26	162·24	5·01
Nitrogen	..	..	6	525·18	16·21
Oxygen	..	..	6	600·00	18·51

From this it appears that the atomic weight of *muriate of nitroharmalidine* is 3696·30, and it consists of—

	Calculated.	Formerly found.
Nitroharmalidine	86·67	
Muriatic acid	12·33	12·14

According to the new formula, the atomic weight of the *platinum double salt* will be 5814·94, and its per-centage composition as follows :—

	Calculated.	Formerly found.
Carbon	33·59	34·21
Hydrogen	3·00	3·08
Nitrogen	9·03	
Oxygen	10·32	
Chlorine	22·87	
Platinum	21·19	21·09

The *acid sulphate of nitroharmalidine* has the atomic weight 4467·00, and the following composition :—

	Calculated.	Formerly found.
Nitroharmalidine	72·54	72·77
Sulphuric acid	22·42	21·98
Water.....	5·04	

For the compound of *nitroharmalidine* with *oxide of silver* we get the atomic weight 4690·20, and it contains in 100 parts—

	Calculated.	Formerly found.
Nitroharmalidine	69·09	68·44
Oxide of silver	30·91	30·00

Lastly, *hydrocyannitroharmalidine* will have the atomic weight 3579·32, and consists of—

	Calculated.	Formerly found.
Nitroharmalidine.....	90·535	
Hydrocyanic acid	9·465	8·85

Bull. de St. Pétersb. Class. Phys.-Math., xii. No. 2, p. 17.

Note on Platinum accompanying Silver in Solution in Nitric Acid. *By* Henry How*.

Having occasion recently to reduce some silver for use in the laboratory of Professor Anderson, in Glasgow, from the collection of precipitates and filters preserved for the purpose, I observed a phænomenon, which, so far as I am aware, has not been noticed, and which I make known to the Society in the hope of some of its members being able to afford further information on the subject. It is a well-known fact that platinum in alloy with silver does dissolve in nitric acid, but I have not been able to meet with an account in any analytical work of what I observed as to its behaviour when so dissolved.

Among the precipitates and filters alluded to, although it was intended that none but salts of silver should be present, it appears from the facts I am about to state, some containing platinum mixed with silver, the results of certain investigations of Professor Anderson, had been introduced. I set about obtaining the silver in the usual way, by drying up and burning the mass of residues and paper in an iron dish, and subsequently fusing the charred mass with carbonate of soda and some borax, to dissolve any iron which might have scaled off from the said dish. A button of silver was obtained, which I proceeded to treat with nitric acid. I was surprised to find a blackish-brown powder remain undissolved, while the whole of the silver, and it alone, as I thought, went up in the acid. On examining the powder, I found it to contain silver, but in what state of combination I could not determine; at the time I imagined it to be a boride, but I am now inclined to think it must have contained platinum. I regret, from what I observed afterwards, I did not submit it to a more rigorous analysis.

The acid solution of the supposed pure silver was evaporated to

* Communicated by the Author.

complete dryness, and gently heated to expel the excess of nitric acid; the residue was then dissolved in a comparatively small quantity of water, as a strong solution was desired; a little yellowish-brown powder remaining undissolved, the fluid was filtered. On diluting a small portion of this liquid with distilled water, I was surprised at seeing a white precipitate fall, and was disposed to imagine that by some inadvertence some salts of bismuth or antimony had been thrown among the silver residues; however, neither of these metals could be detected. The whole fluid was then diluted, and allowed to stand a day; a precipitate formed, from which the solution was poured off, and again allowed to stand. It had rather a turbid appearance, and I observed a sediment gradually form in the shape of pale yellow amorphous flocks, which went on increasing; after about a week, this was collected on a filter, washed with water, and examined. The sediment was found to dissolve completely in ammonia, and for the most part in acetic and in nitric acid. In these acid solutions hydrochloric acid gave a large precipitate, which proved to be chloride of silver; and in the fluid separated from this, platinum was found to be present in abundance. Although I did not certainly detect nitric acid, I am disposed to imagine, from the nature of the process by which it was obtained, that this sediment must have been some basic double salt of silver and platinum with nitric acid, the liquid from which it deposited having an acid reaction. I may mention, that, it being found that platinum was present, I precipitated the whole of the silver in the remaining fluid by hydrochloric acid, and reduced it after washing by iron, and so succeeded in obtaining a pure salt of silver.

I have ventured to offer this note to the Society, as containing a fact, I believe, new and worthy of consideration in cases of analysis where silver and platinum may occur together in an alloy; as, without any intimation of the existence of such a compound as that which spontaneously deposits from an aqueous solution of nitrate of silver containing platinum, the analyst may be as much surprised as I was to observe its formation, and unable to account for it at once. I also think the brown powder, which I have described as remaining after the solution of the alloy by digestion in ordinary nitric acid, is worthy of attention and further notice.—*Quarterly Journal of the Chemical Society.*

On the Combinations of Boracic Acid and Water with Alumina. *By* H. Rose.

When cold solutions of potash-alum and neutral borate of soda (NaO, BO^3), the latter in excess, are mixed together, a very voluminous precipitate is obtained; this is of similar composition with that produced by borate of soda in a solution of oxide of iron. If it be left unwashed, but pressed between blotting-paper immediately after filtration, it consists essentially of $3(Al^2 O^3, BO^3 + HO) + (NaOBO^3 + 2HO)$, mixed with some sulphate of potash. It appears that in this precipitate the neutral borate of soda really forms a

chemical compound with the borate of alumina, as it attracts no carbonic acid.

The salts are however united by so slight an affinity in this compound, that it may be decomposed even by washing with cold water. The water extracts the whole of the borate of soda and half the boracic acid from the borate of alumina. After washing, the compound has the following constitution:—$(Al^2O^3\ BO^3+2HO)+(HO)^3\ Al^2O^3$.

If, instead of neutral borate of soda, the biborate be employed in excess for the precipitation of the alum, and the solutions be mixed cold, a very voluminous precipitate is obtained; this contains biborate of soda and a borate of alumina, which contains more boracic acid than that produced by the neutral borate of soda. Dried at 212° F., its composition is $4(Al^2O^3\ 2BO^3+3HO)+3HO+NaO\ 2BO^3+5HO$, mixed with 1 atom NaO, SO^3, or KO, SO^3. If objections should be raised to the supposition that the compound contains borate of alumina, $Al^2O^3, 2BO^3$, together with hydrate of alumina, $3HO, Al^2O^3$, the composition of the precipitate may also be expressed by $3(Al^2O^3\ 2BO^3+4HO)+2(Al^2O^3, BO^3+HO)+NaO, 2BO^3+5HO$.

When washed with cold water, the compound loses the biborate of soda, and the borate of alumina seven-twelfths of the boracic acid contained in it. The washed compound, when dried at 212° F., had the composition $2(Al^2O^3\ BO^3+2HO)+3HO+Al^2O^3$.—*Bericht der Akad. der Wiss. zu Berlin*, p. 51.

On the Nitrates of Iron. *By* S. Hausmann.

The author has carefully investigated Schönbein's nitrate of iron in Fresenius's laboratory. The acid nitrate of iron was prepared by evaporating the reddish-brown solution of iron in nitric acid to the consistence of a syrup, and then adding half its volume of nitric acid. The crystals which form are—

Neutral Nitrate of Iron, $Fe^2O^3, 3NO^5+12HO$.—Prismatic crystals, fusing at 95° F. Ordway (Chem. Gaz., vol. viii. p. 61) gave the formula $Fe^2O^3, 3NO^5+18HO$ for it. Analysis:—

Fe^2O^3	21·47	1 =	80	22·85
NO^5	46·78	3	162	46·29
HO	31·75	12	108	30·86

When the very concentrated solution of nitrate of iron is mixed with as much water as will reduce its dark red colour to a pale reddish-yellow, boiled and mixed, after cooling, with nitric acid, we obtain the

Basic Salt, $8Fe^2O^3, 2NO^5, 3HO$, in the form of an ochre-yellow precipitate, which is difficult of solution in cold dilute nitric acid, but dissolves readily in water, forming a deep red fluid. The salt, washed with water containing nitric acid, furnished on analysis—

Fe^2O^3	81·92	8 =	640	82·58
NO^5	14·47	2	108	13·93
HO	3·61	3	27	3·49

Basic Salt, $36Fe^2O^3, NO^5+48HO$.—When the concentrated solution of nitrate of iron, containing a little excess of acid, is boiled for a considerable time, a precipitate resembling the preceding is formed; its analysis gave—

Fe^2O^3	85·44	36 =	2880
NO^5	1·61	1	54
HO	12·95	48	432

Basic Salt, $8Fe^2O^3, NO^5+12HO$, was obtained by treating an excess of iron with nitric acid; it forms a rust-coloured precipitate, which is difficult of solution in nitric acid, but dissolves more readily in water. Its analysis gave—

Fe^2O^3	80·33	8 =	640	79·81
NO^5	6·19	1	54	6·73
HO	13·48	12	108	13·46

Ann. der Chem. und Pharm., lxxxix. p. 109.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of Dammara Varnish. By W. Münzel.

If dammara resin be dissolved in cold oil of turpentine, a milk-white turbid varnish is obtained; this turbidity however does not depend upon the incomplete solution of the resin, but rather upon the moisture adherent to it. This moisture, as well as the water enclosed in the interior of the resin, especially in the white opake pieces, produces many defects in the varnish, as when it is prepared cold this water remains in it in a finely-divided state. When such a varnish as this is laid on, the water contained in it, although in such small quantity, can neither evaporate nor soak into the varnished object; and thus these minute water-bubbles produce a dull, rough appearance on the surface of the varnish, so that the latter can never produce a truly glass-like coating. At every change of temperature, these watery particles either expand or contract, until at last, from frequent repetition of this process, or in consequence of a greater elevation of temperature than usual, the coat of varnish bursts or cracks, and falls off as a scaly powder. In order to get rid of this defect entirely, the water adherent to the resin must be completely removed. This is best done by boiling the resin with the oil of turpentine in an open vessel, as in this case the water enclosed in the resin is dissipated below the boiling-point of the oil. The object is equally attained when the resin is well dried in a drying oven before solution, and then dissolved in cold oil of turpentine; if the resin were sufficiently dried, a perfectly clear transparent varnish is obtained, possessing all the properties of a good varnish; this mode of preparation, however, from its complicated nature, is not to be recommended for adoption on the large scale. If a very

small quantity of water be added designedly to a perfectly clear and well-boiled varnish, and the whole is shaken, the latter immediately acquires the turbid appearance, and all the properties of a bad varnish.

In the preparation of dammara varnish, the author employs enamelled cast-iron pots, capable of containing about 50 lbs.; in these, 25 to 30 lbs. of varnish may be conveniently prepared. The dammara resin is put into the pots in a solid state (the powdering of the resin is disadvantageous, as when in this state it forms a mass during the fusion, and the varnish thus generally acquires a colour), the proper quantity of turpentine (5 parts to 4 parts of resin) is then poured to it, and the whole put upon the fire. As soon as the boiling of the oil begins, the water originally included in the resin is dissipated in the form of vapour, and the resin acquires a softer consistence. When all the water is expelled and the oil (or varnish) boils quietly, the solution is completed, and the vessel may be removed from the fire. As long as even traces of water exist in the varnish, its boiling is attended with a bubbling movement; but as soon as all the water is got rid of, the varnish boils quite quietly. That even a very small quantity of water is sufficient to produce this bubbling, may be shown by blowing with the mouth into some quietly-boiling varnish, when the mass immediately appears ready to boil over, entirely in consequence of the slight moisture introduced into it by the breath.

When the varnish is prepared, it is poured through a fine wire sieve, and then allowed to settle sufficiently. Filtration through pointed bags, as recommended by Miller, appears to the author to take up a great deal too much time, is unquestionably attended with loss, and does not lead to the desired object so well as standing quietly.

By this method, two workmen in the author's factory prepare 4–5 cwts. of good varnish per day.

If it be desired to give the varnish a tougher consistence, 2–3 per cent. of good bleached linseed-oil (not boiled with oxide of lead) must be added to it before boiling. This communicates great toughness to it, and it then resists friction, &c. much better.—*Polytechnisches Centralbl.*, 1854, p. 168.

On the Preparation of Iodide of Potassium. By A. Overbeck.

The author gives the following prescription for the preparation of iodide of potassium:—

Iodide of formyle is prepared from 3 equivs. alcohol, 6 equivs. iodine and 5 equivs. potash. If 4 equivs. of iodine be employed to $C^4 H^6 O^2$, the mass thickens too much by separation of the iodide of formyle produced, so that the greater addition of alcohol is very essential to the facilitation of the operation. This is performed in the following manner:—

The necessary quantity of watery alcohol ($C^4 H^5 O$, HO) is first gently heated in a beaker or flask; the dry iodine and the potash

(the latter dissolved in as little water as possible) are then alternately added, in such a manner that before each addition of iodine the solution is completely decolorized. The iodide of formyle produced separates for the most part during the operation in citron-yellow laminæ; its complete separation is effected by pouring over it 20 times as much water as there was alcohol employed; the whole is then collected on a filter, pressed between blotting-paper, and boiled with solution of potash (1 equiv. of iodide of formyle to 4 equivs. potash) until it is completely decomposed into formiate of potash and iodide of potassium.

This fluid, mixed with that filtered from the iodide of formyle, is now evaporated to dryness, then mixed with some powdered charcoal (for the more ready decomposition of any iodate of potash that may have been formed), and heated to redness; the mass, which contains iodide of potassium and carbonate of potash, is then extracted either directly with alcohol, or with water after neutralization by hydriodic acid. Pure iodide of potassium is obtained by crystallization from either of these extracts.—*Archiv der Pharm.*, lxxvii. p. 8.

PROCEEDINGS OF SOCIETIES.

Royal Institution.

March 31, 1854.—On Chemical Affinity among Substances in Solution. By John Hall Gladstone, Esq., Ph.D., F.R.S.

An historical sketch of the development of the ideas of chemists concerning "affinity" was first given. The dogma of Hippocrates that "like combines only with like," was shown to be superseded by the view of Glauber and others, that unlike substances combine most readily; and that where two bodies have an affinity *for* one another, it is a sign that they have *no* affinity *with* one another. The views of Newton and Boyle in reference to the different degrees of strength of affinity were then considered, and particular attention was directed to the doctrine of Bergmann, that when a decomposition takes place by means of the greater elective attraction of a third body, that decomposition is complete. In opposition to this, Berthollet contended that in all such cases of composition or decomposition there takes place a partition of the base, or subject of the combination, between the two bodies whose actions are opposed; and that the proportions of this partition are determined, not solely by the difference of energy in the affinities, but also by the difference of the quantities of the bodies—by their physical condition,—and by that of the combinations capable of being generated. These views did not meet with a favourable reception at the time of their promulgation; and the attention of chemists had been drawn away from the subject until within these last few years, when Malaguti, Bunsen, Debus, and Williamson have published investigations bearing upon the point. The lecturer then stated, that before any of

these papers had appeared, he had been thinking of and performing some experiments upon the subject in question, and that he was still continuing them.

After a few experiments illustrative of "chemical combination" and of "elective affinity," others were introduced to show how easily this latter phænomenon was affected by circumstances. Thus ammonia will displace alumina from a solution of the sulphate, but on the other hand, alumina will displace ammonia when heated with the solid sulphate of that volatile base; whilst if solutions of chloride of aluminium and sulphate of ammonia be mixed and evaporated, crystals of the double sulphate, ammonia-alum, will appear. There were on the table two white salts; the one had been carbonate of baryta, but by boiling with excess of sulphate of potash, it had been converted into the sulphate; the other had been sulphate of baryta, but by long-continued boiling with much carbonate of potash, it had suffered the opposite change into the carbonate. The lecturer then stated that so great is the influence exerted by these various circumstances, that some have doubted whether there be a true "elective affinity;" he however believed that after making every allowance for known causes there is still a residuary phænomenon to which that name is the most appropriate. Allowing then, with Bergmann, that relative degrees of affinity exist, the question arises:— Is Berthollet's law also correct? It is very difficult to arrive at a satisfactory answer, since it is almost impossible to eliminate other influences. Several reactions, however, were mentioned as tending to show that there is some truth in the law:—for instance, the solution of gold in hydrochloric acid upon the addition of nitrate of potash. The experiments of Bunsen on mixtures of carbonic oxide and hydrogen, exploded with a quantity of oxygen insufficient for complete combustion; and those of Debus on the precipitation of mixed hydrates of lime and baryta by carbonic acid were explained; as also the remarkable fact noticed by both, that the resulting products were always in certain atomic proportions to one another. But in both these cases the first products of the chemical action are removed at once from the field: it is quite another case when they remain free to act and react on one another. Supposing they all remain in solution, the requisite is fulfilled; but how are we to know what has then taken place? Malaguti thought to obtain an indication of this by mixing the aqueous solutions of two salts, one of which is soluble in alcohol, and the other is insoluble, and then pouring them into very strong alcohol, and analysing the salts immediately thrown down. His results are tabulated; they are valuable, but to some extent open to objection, on account of the disturbing influence of the alcohol. Some observations of Professor Graham, and others of Professor Williamson, as yet unpublished, were then spoken of, and the Lecturer proceeded to describe his own endeavours to arrive at a knowledge of the intimate constitution of a mixture of salts in solution by observing their physical properties, especially colour.

If solutions of one equivalent of nitrate of iron, and a triple equi-

valent of sulphocyanide of potassium be mixed, a blood-red colour results owing to the formation of sulphocyanide of the sesquioxide of iron; the question arises—Has all the iron left the nitric acid to unite itself with the sulphocyanogen? It has not; for on the addition of equivalent after equivalent of sulphocyanide of potassium, a deeper red is constantly obtained. The arrangement by which this deepening of colour was quantitatively determined was explained, and imitated on the lecture table. The result was that even up to 375 equivalents, a regular increase was observed to take place, more rapidly at first than afterwards, which was exhibited to the eye by the results being projected as a curve. Again, as in the mixture of equal equivalents of the two salts, some iron still remains in combination with the nitric acid, a portion of the potassium must still remain united to the sulphocyanogen. Accordingly the addition of more iron salt also gives a deeper colour. The curve expressing the results of this experiment was a regular continuation of the curve formerly mentioned; and neither of them exhibited any of those sudden transitions which the experiments of Bunsen and Debus present. Diagrams exhibiting curves of the gallate and meconate of iron were also exhibited. Various experiments were then performed, showing the alteration in the resulting colour upon any change of any of the elements in the primary experiment; for instance, the substitution of other acids for the nitric acid, or of other bases for the potash. On the addition of a colourless salt to a coloured one, there results a diminution of the colour greater than the mere dilution would have produced, as was exemplified in the cases of the red sulphocyanide of iron mixed with sulphate of potash, and of the scarlet bromide of gold mixed with chloride of potassium. The lecturer accordingly drew the conclusion that when two salts mix without precipitation or volatilization, the acids and bases frequently, if not universally, arrange themselves according to some definite proportion; and that this depends on the relative quantity of the two salts, as well as upon the proper affinities of the substances composing them. He was unable then to enter upon the influence of heat, or of dilution in certain cases, or to add any remarks connected with double salts, or with other metals, or upon certain practical applications of these views in chemical and physiological science.

The fact that we very frequently find the double decomposition of a salt to be *complete*, the *whole* of one of its constituents being precipitated, was shown to be easily explained on the principles of Berthollet. Thus, for instance, when chromate of potash and nitrate of silver are mixed, at the first moment a division will take place producing four salts, but one of these — the chromate of silver—is thrown down at once as a precipitate, and thus put out of the field of action. Another division of the acids with the bases must take place, producing of course more of the insoluble chromate, and so on, till at length the whole of the silver is removed. And that this is really what does take place is rendered almost certain by the fact that wherever by an interchange of acids and bases a precipitate can be produced, that precipitate does form; and, if the

substance be perfectly insoluble, the whole is thrown down; this occurring in opposition to all rules of "affinity," and to all tables that Bergmann, or any other chemist, ever did or could construct. The volatility of one of the products acts in the same manner as insolubility, as is exemplified in the decomposition of carbonates by any other acid. Crystallization also is but another phase of the same phænomenon. An experiment was exhibited in illustration of this. Dilute solutions of nitrate of lime, and sulphate of soda, were mixed at the ordinary temperature without producing any separation of solid matter; but they were so proportioned that upon heating the mixture, the crystallization of some sulphate of lime was determined, and when once this had commenced, it progressed rapidly; resembling in that respect the ordinary phænomena of precipitation. If in a double decomposition a far larger quantity of a sparingly soluble salt be produced at the first moment than the water can dissolve, the crystals will be formed rapidly and will accordingly be very small in size; but should there be formed at once only just sufficient to determine a separation in the solid form, the crystals will grow gradually, and will often attain a large size. This was exemplified on the mixture of nitrate of silver with the sulphates of copper and of potash respectively.

It is possible that the law of Berthollet may not be universally applicable; yet the present advanced state of science shows that not only is there, as Bergmann insisted, a true chemical affinity, that is, a preference of one substance to combine with a certain other substance instead of a third, but, in a great number of instances at least, this substance will combine with both according to certain proportions, whenever the whole of the affinities can be brought into play at the same time.

April 7.—On Silica and some of its applications to the Arts. By the Rev. J. Barlow, M.A., F.R.S., Vice-President, and Sec. R.I.

Silica is one of the most abundant substances known. Quartz, common sand, &c., flint, chalcedony, opal, &c., and a variety of sand described by Mr. J. T. Way*, may respectively be taken as examples of crystallized and uncrystallized silica. Under all these forms silica is capable of combining with bases as an acid. Heat is however essentially necessary to effect this combination, a combination of which all the well-known silicates, whether natural, as felspar, mica, clay, &c., or artificial, as glass, slags, &c., are the results. The common forms of insoluble glass are produced by the union of silica with more than one base. But, when combined with an alkaline base only, silica forms a soluble glass, the degree of solubility of which depends on the proportion which the silicic acid bears to this alkaline base . . . . This soluble silicated alkali (or water-glass) may be prepared by various processes. If sand be used, 15 parts of fine sand, thoroughly incorporated with 8 parts of carbonate of soda, or with ten of carbonate of potash, and one of

* Quarterly Journal of Chemical Society, July 1, 1853, and Journal of Royal Agricultural Society, vol. xiv. part 1.

charcoal fused in a furnace, will produce a silicated alkali which is soluble in boiling water. Messrs. Ransomes obtained this silicated alkali by dissolving broken flints in a solution of caustic alkali at a temperature of 300° Fahr. And more recently, Mr. Way has observed that the sand which he has described will combine with caustic alkali at boiling heat, also producing a water-glass.

This water-glass has been applied to several important purposes, three of which were specially noticed.

I. *To protect Building-stones from decay.*—The stone surfaces of buildings, by being exposed to the action of the atmosphere, become liable to disintegration from various causes. Moisture is absorbed into their pores. The tendency of their particles to separate, in consequence of expansion and contraction, produced by alternation of temperature, is thus increased. Sulphurous acid is always present in the atmosphere of coal-burning cities, and cannot but corrode the calcareous and magnesian ingredients of oolites and dolomites. It is true that good stone resists these sources of injury for an indefinite time, but such a material is rarely obtained. As a preventive of destruction, whether arising from physical or chemical causes, it has been proposed to saturate the surfaces of the stones with a solution of the water-glass.

It is well known that the affinity of silica for alkali is so feeble that it may be separated from this base by the weakest acids, even by carbonic acid. According to the expectation of those who recommend the silification of stone, the carbonic acid of the atmosphere will set the silica free from the water-glass, and the silica, thus separated, will be deposited within the pores and around the particles of the stone. The points of contact of these particles will thus be enlarged, and a sort of glazing of insoluble silica will be formed, sufficient to protect the stone against the effects of moisture, &c. This cause of protection applies chiefly to sand-stones. But wherever carbonate of lime or carbonate of magnesia enters notably into the composition of the building-stone, then an additional chemical action, also protective of the stone, is expected to take place between these carbonates and the water-glass. Kuhlmann remarks, "Toutes les fois que l'on met en contact un sel insoluble avec la dissolution d'un sel dont l'acide peut former avec la base du sel insoluble un sel plus insoluble encore, il y a échange; mais le plus souvent cet échange n'est que partiel*." In consequence of this "partial exchange" an insoluble salt of lime may be looked for whenever a solution of water-glass is made to act on the carbonate of lime or carbonate of magnesia existing in oolitic or dolomitic building-stones.

This expectation, however, has not been altogether sanctioned by experiment. A gentleman, eminently conversant with building materials†, immersed a piece of Caen-stone in a solution of silicate of potash in the month of January 1849. This fragment, together

* Expériences Chimiques et Agronomiques, p. 120.

† Charles H. Smith, Esq., one of the authors of the 'Report on the Selection of Stone for the Building of the New Houses of Parliament.'

with a portion of the block from which it had been separated, was placed on the roof of a building in order that it might be fully exposed to the action of atmosphere and climate. After five years the silicated and the unsilicated specimens were found to be both in the same condition, both being equally corroded. These specimens were exhibited in the Theatre of the Institution. But whatever ultimate results may ensue from this process, the immediate effects on the stone are remarkable. Two portions of Caen-stone were exhibited, one of which had been soaked in a solution of water-glass two months before. The surface of the unsilicated specimen was soft, readily abraded when brushed with water, and its calcareous ingredients dissolved in a weak solution of sulphurous acid. The silicated surface, on the other hand, was perceptibly hard, and resisted the action of water and of dilute acid when similarly applied*.

II. Another proposed use of the water-glass is that of *hardening cements, mortar,* &c., so as to render them impermeable by water.

Fourteen years since Anthon† of Prague proposed several applications of the water-glass. Among others he suggested the rendering mortars water-proof. He also suggests that this substance might be beneficially employed as a substitute for size in white-washing and staining walls. It was demonstrated by several experiments that carbonate of lime, mixed up with a weak solution of water-glass, and applied as a whitewash to surfaces, was not washed off by sponging with water, and that common whitewash, laid on in the usual manner with size, was rendered equally adhesive when washed over with water-glass.

III. *The Stereochrome of* Fuchs.—The formation of an insoluble cement by means of the water-glass, whenever the carbonic acid of the atmosphere acts on this substance, or whenever it is brought in contact with a lime-salt, has been applied by Fuchs to a most important purpose. The stereochrome is essentially the process of fresco secco‡ invested with the capability of receiving and perpetuating works of the highest artistic character, and which may be executed on a vast scale. Fuchs's method is as follows§:—

"Clean and washed quartz-sand is mixed with the smallest quantity of lime which will enable the plasterer to place it on the wall. The surface is then taken off with an iron scraper, in order to remove the layer formed in contact with the atmosphere; the wall being still moist during this operation. The wall is then allowed to dry; after drying it is just in the state in which it could be rubbed off by the finger. The wall has now to be *fixed, i. e.* moistened with

* Silliman's American Journal, January, 1854, contains a notice of the application of the water-glass to the decaying surfaces in the Cathedral of Nôtre Dame in Paris.

† Neuere Mittheilungen über die Nutzanwendung des Wasser-Glases, 1840. This subject has also been fully treated by Kuhlmann in his 'Mémoire sur l'Intervention de la potasse ou de la soude dans la formation des chaux hydrauliques,' &c., 1841.—*Expériences Chimiques et Agronomiques.*

‡ Vide Eastlake's Materials for a History of Oil Painting, p. 142.

§ These particulars were obtained by Dr. Hofmann from Mr. Echter. A stereochromic picture by Echter and a sample of the water-glass as prepared in Munich were also exhibited by Dr. Hofmann.

water-glass*. [An important point is not to use too much water-glass in moistening the wall.] This operation is usually performed with a brush. The wall must be left in such a condition as to be capable of receiving colours when afterwards painted on. If, as frequently happens, the wall has been too strongly fixed, the surface has to be removed with pumice and to be fixed again. Being fixed in this manner the wall is suffered to dry. Before the painter begins, he moistens the part on which he purposes to work with distilled water, squirted on by a syringe. He then paints: if he wishes to repaint any part, he moistens again. As soon as the picture is finished, it is syringed over with water-glass. After the wall is dry, the syringing is continued as long as a wet sponge can remove any of the colour. An efflorescence of carbonate of soda sometimes appears on the picture soon after its completion. This may either be removed by syringing with water, or may be left to the action of the atmosphere." Not to dwell on the obvious advantages possessed by the stereochrome over the real fresco (such as its admitting of being retouched and its dispensing with joinings), it appears that damp and atmospheric influences, notoriously destructive of real fresco, do not injure pictures executed by this process.

The following crucial experiment was made on one of these pictures. It was suspended for twelve months in the open air, under the principal chimney of the New Museum at Berlin; "during that time it was exposed to sunshine, mist, snow, and rain," and nevertheless "retained its full brilliancy of colour."

The stereochrome has been adopted on a grand scale by Kaulbach in decorating the interior of the great national edifice at Berlin already alluded to. These decorations are now in progress, and will consist of historical pictures (the dimensions of which are 21 feet in height and $24\frac{3}{4}$ in width), single colossal figures, friezes, arabesques, chiaro scuro, &c. On the effect of the three finished pictures, it has been remarked by one whose opinion is entitled to respect, that they have all the brilliancy and vigour of oil paintings, while there is the absence of that dazzling confusion which new oil paintings are apt to present, unless they are viewed in one direction, which the spectator has to seek for.

Mr. A. Church has suggested that if the surface of oolitic stones (such as Caen-stone) is found to be protected by the process already described, it might be used, as a natural *intonaco*, to receive coloured designs, &c. for exterior decorations; the painting would then be cemented to the stone by the action of the water-glass.

Mr. Church has also executed designs of leaves on a sort of terra cotta, prepared from a variety of Way's silica rock, consisting of 75 parts clay and 25 of soluble silica. This surface, after being hardened by heat, is very well adapted for receiving colours in the first instance, and for retaining them after silication.

* The composition of the specimen was—

	per cent.
Silica	23·21
Soda	8·90
Potash	2·52

[The specific gravity of the solution 3·81.]

THE CHEMICAL GAZETTE.

No. CCLXXX.—June 15, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some double Salts of Molybdic Acid. *By* H. STRUVE.

THE author has investigated a series of double salts of molybdic and tungstic acids. In this memoir he describes only those of the former acid, remarking however that they are not isomorphous with the salts of tungstic acid.

The following compounds were employed in the preparation of the salts hereafter to be mentioned:—

1. The salt $KO, 3MoO^3 + 3HO$.
2. The salt $NaO, 3MoO^3 + 7HO$.
3. The salt $NH^4O, 3MoO^3 + NH^4O, 2MoO^3 + 3HO$.

If these salts be boiled in great excess with alumina, oxide of chromium, hydrated oxide of manganese, &c., a series of double salts is obtained: the manganese salts are not isomorphous with the others.

Molybdate of Alumina and Potash, $3(KO, 2MoO^3) + Al^2O^3 6MoO^3 + 20HO$.—This salt is obtained by adding freshly-precipitated alumina to a solution of trimolybdate of potash, and boiling the whole for several hours, during which only the water evaporated must be replaced. When a small sample of the solution shows the production of the new salt, either by the formation of microscopic crystals or by furnishing a precipitate with caustic ammonia, the solution is filtered whilst boiling hot. If it be sufficiently concentrated, the new compound crystallizes on cooling in little white, perfectly flat, four-sided prisms; if this be not the case, the solution must be concentrated by heat; when slowly cooled, the salt crystallizes in small distinct cubes. The salt may be purified by recrystallization.

This compound may be more readily produced by the following method:—A solution of common alum is precipitated by any neutral molybdate; a voluminous precipitate is formed, which is a mixture of hydrate of alumina with sulphate and molybdate of alumina, and very probably also contains potash. This precipitate, after it has been well washed, is treated with trimolybdate of potash as above described, when the new salt is formed.

In a pure state this salt consists of small white cubic crystals,

formed of an aggregation of square prisms. At ordinary temperatures it undergoes no change, but at 212° F. it loses 6 equivs., or 4·45 per cent. of water. When more strongly heated over a spirit-lamp, the salt fuses, and solidifies on cooling into a yellowish crystalline mass, which is very difficult of solution in water, and even in acids. The salt itself dissolves very sparingly in water, 100 parts of it requiring 4067 parts of water at 63° F. Analyses:—

Air-dried salt:—

KO	..	..	3 =	1766·7	11·65
Al^2O^3	4·41	..	1	640·8	4·23
MoO^3	..	..	12	10502·4	69·28
HO	14·62	14·94	20	2250·0	14·84

Salt dried at 212° F.:—

KO	11·96	3 =	1766·7	12·19
Al^2O^3	4·83	1	640·8	4·42
MoO^3.....	..	12	10502·4	72·51
HO	..	14	1575·0	10·88

Molybdate of Ammonia and Alumina, $3(NH^4O, 2MoO^3) + Al^2O^3, 6MoO^3 + 20HO$.—For the preparation of this salt, a solution of any molybdate of ammonia is boiled with hydrate of alumina. The alumina is gradually dissolved, with loss of ammonia. This salt is formed much more readily than the potash salt.

Like the potash salt, it crystallizes in small, square, shining, white prisms, which readily lose as much as $6\frac{1}{2}$ equivs., or 5·09 per cent. of water, when exposed to the air; at 212°–248° F. they part with another $7\frac{1}{2}$ equivs. without losing any of their lustre. The last 6 equivs. of water are only dissipated at a higher temperature. When heated with a spirit-lamp, water and ammonia are driven off, whilst the residue, which is of a yellowish colour, retains the form of the crystals, and contains molybdic acid and alumina. It is more readily soluble in water than the potash salt. Analyses:—

Air-dried salt:—

NH^4O	..	..	3 =	975·0	6·79
Al^2O^3 }	77·55	78·34	1	640·8	4·46
MoO^3 }			12	10502·4	73·09
HO.....	..	..	20	2250·0	15·66

Salt dried at 248° F.:—

NH^4O	13·18	13·87	3 =	975·0	7·62
Al^2O^3.....	5·13	5·14	1	640·8	5·01
MoO^3	..	81·30	12	10502·4	82·10
HO.....	..	..	6	675·0	5·27

Molybdate of Potash and Oxide of Chromium, $3(KO, 2MoO^3) + Cr^2O^3, 6MoO^3 + 20HO$.—This salt is formed under the same conditions as the salts of alumina, by boiling hydrated oxide of chromium with trimolybdate of potash.

It forms beautiful rose-coloured prisms, which undergo no change

on exposure to the air; when heated, it fuses, and solidifies on cooling in a crystalline form, with a greenish-red colour, when it is very difficult of solution in water and acids. 100 parts of the salt require 3851 parts of water at 63° F. for their solution. If the solution of this salt be precipitated with a solution of silver, a white amorphous precipitate with a reddish tinge is obtained; this contains oxide of chromium, as well as oxide of silver and molybdic acid. When washed with water, this precipitate is decomposed, as is the case with the molybdates of silver in general. At 212° F. it loses 10 equivs., or 7·27 per cent. of water. Analysis:—

KO Cr^2O^3 MoO^3	85·46	6·25	..	..	3 1 12	1766·7 957·8 10502·4	11·41 6·19 67·86
HO	..	14·05	14·37	14·36	20	2250·0	14·54

Molybdate of Ammonia and Oxide of Chromium, $3(NH^4O, 2MoO^3) + Cr^2O^3, 6MoO^3 + 20HO$.—This salt is prepared like the corresponding salt of alumina. It crystallizes in small, quadratic, rose-coloured prisms. When dried at 212° F., it loses 10 equivs., or 7·66 per cent. of water; at 248° F., 2 equivs. more are driven off, so that on the whole it loses 12 equivs., or 9·19 per cent. of water at 248° F. After heating to redness, a mixture of oxide of chromium and molybdic acid remains. Analysis:—

NH^4O	..	3 =	975·0	6·64
Cr^2O^3	6·78	1	957·8	6·52
MoO^3	72·11	12	10502·4	71·52
HO	..	20	2250·0	15·32

Molybdate of Soda and Oxide of Chromium, $3(NaO, 2MoO^3) + Cr^2O^3, 6MoO^3 + 21HO$.—This salt is obtained by boiling hydrated oxide of chromium with trimolybdate of soda. It forms microscopic four-sided prisms, of a lilac colour, which readily effloresce in the air, and acquire thereby a paler colour. It is very soluble in water. At 212° F. it loses 12 equivs., or 9·01 of water; when more strongly heated, it fuses, and solidifies on cooling in a crystalline form, and with a darker lilac colour. Analysis:—

NaO	..	3 =	1162·8	7·76
Cr^2O^3	6·71	1	957·8	6·39
MoO^3	..	12	10502·4	70·09
HO	15·88	21	2362·5	15·76

Molybdate of Potash and Iron and Molybdate of Ammonia and Iron.—If a solution of trimolybdate of potash or ammonia be boiled with hydrated peroxide of iron, the oxide is dissolved by degrees, and the solution acquires an orange colour; when this is carefully evaporated, reddish-brown crystalline compounds of oxide of iron, which dissolve readily in water, are first of all obtained. By further evaporation, the double salt is obtained crystallized, but always contaminated with basic compounds. The author did not succeed in preparing this salt in the pure state in sufficient quantities for ana-

lysis; it is extremely probable, however, that it has the same composition as the preceding salts, as it furnishes the same microscopic yellowish-white crystals.

Pentamolybdate of Iron, $Fe^2O^3, 5MoO^3 + 16HO$.—If protosulphate of iron be added to a solution of trimolybdate of potash, a reduction very soon commences, the protoxide of iron extracting oxygen from the molybdic acid. The solution acquires a blue colour, then becomes brown, and this by degrees becomes paler, without however producing any precipitate. But if, when the solution of iron is added, a current of chlorine be passed through the fluid, a voluminous non-crystalline precipitate is instantaneously formed, which is no further changed by chlorine gas; the fluid acquires a greenish-yellow colour. This precipitate, when collected on a filter, may be washed with water, in which it is very sparingly soluble. When dried in the air, it forms a light yellow powder, which loses 12 equivs. or 18·61 per cent. of water at 212° F. When more strongly heated, the compound loses all its water, and acquires a yellowish-green colour. If heated to redness in a platinum crucible, it fuses, with partial volatilization of the molybdic acid. Analysis:—

Fe^2O^3	13·88	1 =	1000·0	13·94
MoO^3	61·59	5	4376·0	60·98
HO	24·53	16	1800·0	25·08

Molybdate of Potash and Oxide of Manganese, $5(KO, 2MoO^3) + Mn^2O^3, 6MoO^3 + 12HO$.—This salt is produced under the same circumstances as the other double salts, namely, by boiling a solution of trimolybdate of potash with hydrated oxide of manganese. The solution gradually becomes of a beautiful red colour, and on the cooling of the filtered solution, shining crystals are deposited; these may be purified by recrystallization.

This salt may be obtained much more readily than by the method just described, by the action of chlorine gas upon molybdate of potash in the presence of protoxide of manganese, in the following manner:—A current of chlorine gas is passed through a hot solution of trimolybdate of potash, and small quantities of a solution of protosulphate of manganese are added from time to time. As long as the chlorine is passed through the solution of molybdate of potash, no change is produced; but as soon as even a small trace of a salt of protoxide of manganese is introduced, the solution instantaneously acquires a reddish colour. When a somewhat larger quantity of protoxide of manganese has been added, the fluid becomes of a deep red colour, and in a short time the separation of the new salt commences, whilst the solution remains deep red. When a fresh addition of the salt of manganese produces no greater intensity of colour, the passage of the chlorine may be stopped. The newly-formed salt settles very quickly to the bottom, so that the supernatant fluid may be poured off, and the salt may be obtained in a pure state merely by washing with cold water. A fresh quantity of the salt separates from the deep red solution whilst cooling, and this is in

rather large crystals. If the solution be afterwards concentrated by a gentle heat, a further quantity of the salt is obtained. The remainder of the fluid however always retains its deep red colour, and contains various other compounds, which the author has not yet investigated, as, on account of the complicated phænomena presented by them, they require a particular study.

This manganese salt forms shining rhombohedra of an orange-red colour; the angle formed by their apical edges $=107° 45'$, as determined by a reflecting goniometer. It is difficult of solution in water, 100 parts requiring 38426 parts of water at 63° F. for their solution; in boiling water it dissolves far more readily, but in this case undergoes partial decomposition, a basic molybdate of manganese being separated in brown flakes. The salt undergoes no change in the air; at 212° F. it loses 9 equivs., or 5·22 per cent. of water; at 320° F. it loses 2 more equivs. of water, so that the entire loss amounts to 11 equivs., or 6·38 per cent. of water; the salt only acquires a somewhat darker colour. If it be exposed to a higher temperature, the remaining equivalent of water is first of all dissipated, and the salt acquires a black colour. If the heat be then raised, the salt fuses, and solidifies on cooling in a crystalline form, and with a reddish-brown colour. When a solution of nitrate of silver is added to a solution of this salt, a voluminous flesh-coloured precipitate is immediately produced, and sinks rapidly to the bottom. But if this be collected on a filter and washed, it is decomposed, and the water becomes milky in passing through the filter. In this respect it behaves exactly like the molybdate of silver already described by Svanberg and the author. This silver salt however contains oxide of manganese, as well as molybdic acid and oxide of silver, so that this precipitate must be regarded as a silver salt corresponding to the potash salt. A similar precipitate is obtained with protonitrate of mercury; this is soluble in a great excess of the saline solution. It is not soluble in an excess of protonitrate of mercury, but the action of this produces a change in it; it gradually contracts to a great extent, acquires a golden-yellow colour, and then consists of small acicular crystals. This conversion is effected still more rapidly at a boiling heat. Analysis:—

KO.....	16·15	16·11	..	5	= 2944·5	15·19
Mn^2O^3 ..	5·00	5·19	..	1	989·4	5·10
MoO^3 ..	72·30	73·61	..	16	14103·2	72·75
HO.....	6·89	6·56	7·20	12	1350·0	6·96

Molybdate of Ammonia and Manganese, $5(NH^4O, 2MoO^3) + Mn^2O^3, 6MoO^3 + 12HO$.—When a solution of molybdate of ammonia is boiled with hydrated oxide of manganese, this salt is produced with the same phænomena as the potash salt, except that in this case the solution of the oxide takes place more rapidly. This salt is isomorphous with the potash salt, and agrees with it in all its properties. It is more readily soluble in water, 100 parts of it only requiring 10172 parts of water at 63° F. for their solution. It undergoes no change by exposure to the air. At 212° F. it loses 9 equivs., or

4·60 per cent.; at 320° F., 11 equivs., or 6·85 per cent. of water. Analysis :—

NH^4O	15·96	5 =	1625·0	8·99
Mn^2O^3	4·85	1	989·4	5·47
MoO^3.....	..	16	14103·2	78·07
HO	..	12	1350·0	7·47

The principal result of the boiling of molybdate of ammonia with hydrated oxide of manganese is the production of the above salt; but besides this, various other salts and double salts containing manganese are produced; these, however, the author has not investigated particularly, and he only makes a few observations upon them.

When, after the formation of the red salt, the undissolved portion is washed, the residue dissolves as soon as no other salts are present, giving a deep brown colour to the water. This solution, when evaporated on the water-bath, furnishes a brownish-black, shining, non-crystalline mass, which is readily soluble in water, from which it is again precipitated in flakes by other salts, as for instance muriate of ammonia. The compound is decomposed by ammonia, oxide of manganese being separated, and molybdate of ammonia remaining in solution. An analysis of the mass, dried at 212° F., led to the conclusion that it was to be regarded as basic molybdate of manganese. Thus the author found that 0·311 grm. of the substance, dried at 212° F., lost 0·046 grm. at a red heat, and 0·192 grm. of oxide of manganese were contained in the residue. This leads to the following composition :—

Mn^2O^3	61·77	2 =	1978·8	59·89
MoO^3.....	23·43	1	875·2	26·49
HO	14·80	4	450·0	13·62

This compound is also formed by the decomposition of the two double salts of manganese by boiling with water, when it separates in brown flakes.

If this compound remains insoluble and amorphous during the formation of the red salt, other crystalline salts are found in the solution. When the solution of molybdate of ammonia, from which the red salt has crystallized, and which possesses a pale brown colour, is further evaporated, which is best done by exposure to the air at the ordinary temperature, the common ammoniacal salt first crystallizes. As the solution becomes more concentrated, a yellowish-white salt separates in distinct crystals; and this, when treated with water, is decomposed into trimolybdate of ammonia and a yellow sparingly soluble salt. Simultaneously with this salt, but in very small quantity in comparison with the other salts, black octahedric crystals make their appearance; these have a strong lustre, and are soluble in water without change. The author can say nothing as to the conditions required for the direct formation of these salts, as he also obtained various other salts by the evaporation of the mother-liquor of the red salt.

Trimolybdate of soda acts in a similar manner towards oxide of

manganese, furnishing yellowish-red crystals, which are very readily soluble in water. The author has not examined this salt more fully.

Molybdate of the Protoxide of Manganese, $MnO, MoO^3 + HO$.—This salt is obtained by treating protocarbonate of manganese with trimolybdate of potash or soda. It forms a heavy white powder, which, when examined by the microscope, is found to consist of prismatic tables. It does not lose its single equivalent of water, either by exposure to the air or by heating to 212° F.; this is only dissipated at a higher temperature, when the salt acquires a pale brown colour. If the protocarbonate of manganese contains oxide of manganese, the salt is obtained of a darker colour, and analysis then shows a larger quantity of protoxide of manganese than is required theoretically. The salt dissolves with great difficulty in boiling water. Analysis:—

MnO	31·41	..	1 =	444·7	31·05
MoO^3	60·85	..	1	875·2	61·10
HO	7·97	7·67	1	112·5	7·85

If this salt be boiled for a long time with a solution of trimolybdate of potash or soda, a double salt of protoxide of manganese is obtained in the solution; this crystallizes when the solution is evaporated. The author has not further examined this compound.

Bimolybdate of the Protoxide of Mercury, $Hg^2O, 2MoO^3$.—When a solution of trimolybdate of potash is precipitated by protonitrate of mercury, a yellowish-white flocculent precipitate is obtained. But the solution always contains protoxide of mercury as well as molybdic acid, so that in this case the precipitation of the molybdic acid takes place very imperfectly. If the precipitate be immediately collected on a filter, the wash-water is milky on passing through the filter, and the precipitate contracts a little. If the washing be stopped, when a drop of the filtrate, evaporated and heated to redness on platinum foil, no longer leaves a residue, the filter contains the bimolybdate of the protoxide of mercury. But if the washing be continued, the precipitate gradually acquires a beautiful golden-yellow colour, and becomes converted into microscopic acicular crystals of neutral protomolybdate of mercury. This conversion goes on more rapidly when, after the precipitation of the trimolybdate of potash by the mercurial solution, the whole is boiled, or even left to stand for some time.

The bimolybdate of the protoxide of mercury is an anhydrous, amorphous, yellowish-white precipitate; when heated to redness, it is decomposed into molybdic acid, mercury and oxygen. Analysis furnished:—

Hg^2O	..	1 =	2600·0	59·76
MoO^3	39·63	2	1750·4	40·24

Basic Molybdate of Copper, $4CuO + 3MoO^3 + 5HO$.—For the preparation of this compound, a concentrated solution of the molybdate of ammonia ($= NH^4O, 3MoO^3 + NH^4O, 2MoO^3 + 3HO$) is added to a boiling solution of sulphate of copper, when a heavy, green,

non-crystalline powder is quickly deposited. This precipitate must be immediately collected upon a filter, as otherwise it is contaminated by other basic compounds. The filtrate, when evaporated, furnishes first of all a further quantity of this salt, but mixed with another of a lighter colour. On further evaporation, a double salt separates, which will be described below.

This salt, when dried in the air, contains 5 equivs. of water, of which it loses 3 equivs., or 6·52 per cent., at 212° F., without its colour undergoing any change. At a higher temperature it loses the remaining 2 equivs. of water, when the colour changes to dark brownish-red. When water is poured over the anhydrous salt, it is gradually taken up by it. Analysis:—

CuO		38·88	4 =	1986·4	38·39
MoO^3		49·96	3	2625·6	50·74
HO	10·75	..	5	562·5	10·87

Molybdate of Ammonia and Copper, CuO, $2MoO^3 + NH^4O$, $3MoO^3 + 9HO$.—This salt is formed, as already stated, during the evaporation of the filtrate of the preceding salt; it is however almost always contaminated by an acid molybdate of ammonia, from which it may be separated by solution in boiling water. This salt is most readily obtained by adding an excess of molybdate of ammonia to a solution of sulphate of copper, both cold. A bluish-white crystalline salt is pretty rapidly separated, which when examined by the microscope is found to consist of small rhombic crystals. It is difficult of solution in cold water; it dissolves without decomposition in boiling water, and may be recovered unchanged by evaporation. The air-dried salt contains 9 equivs. of water; at 212° F. it loses 4 equivs., or 7·25 per cent., and at 266° F. 4 equivs. more, making 8 equivs., or 14·49 per cent. of water. Water and ammonia are driven off by a stronger heat, and a yellowish mass is left, which fuses when strongly heated, and loses traces of molybdic acid. Analysis:—

CuO	7·64	..	1 =	496·6	7·99
MoO^3	..	..	5	4376·0	70·46
NH^4O }	.. 22·09	21·59	1	325·0	5·23
HO }			9	1012·5	16·32

Bull. de St. Pétersb. Cl. Math.-Phys., xii. p. 142.

On Caprylic Alcohol and its Derivatives. By J. Bouis.

Caprylic alcohol, $C^{16}H^{18}O^2$, is a transparent, colourless, oleaginous liquid, producing stains upon paper like the essential oils; it is insoluble in water, but soluble in ordinary alcohol, in wood-spirit, æther and acetic acid; it readily dissolves fatty substances, resins, sulphur, phosphorus and iodine. It burns with a fine white flame, and has no action upon the plane of polarization; its density is 0·823 at 63° F.; it boils at 354° F., without decomposition, under a pressure of $0·760^{mm}$.

Sulphuric acid converts it into sulphocaprylic acid, which is

capable of combining with bases, or into a fluid carburet of hydrogen isomeric with olefiant gas, amylene, &c. This carburet is also produced by fused chloride of zinc.

Caprylic alcohol is attacked by potassium and sodium, furnishing compounds in which a portion of the hydrogen is replaced by the metal. Chloride of calcium combines with it, furnishing well-defined crystals; this compound is more soluble in the cold than by heat, and is decomposed by water.

Castor-oil, when suitably treated by potash, always furnishes one-fourth of its weight of sebacic acid and one-fourth of its volume of perfectly colourless alcohol; the residue consists of a mixture of fatty acids, one fluid, resembling oleic acid, the other solid, and presenting the composition of æthalic acid. The alcohol, when purified by repeated distillation from fragments of potash, may be distilled completely without acquiring any colour, and without any variation in its boiling-point.

Numerous analyses, performed with products obtained from American, French and German oils, agreed exactly with the formula

$$C^{16}\,H^{18}\,O^{2}=4 \text{ vols.},$$

which is also confirmed by several determinations of the density of the vapour. Identical results were obtained with the alcohol produced by treating pure ricinolic acid with potash.

Caprylene, $C^{16}\,H^{16}$, is a colourless refractive fluid, with a rather strong odour, which is insoluble in water, but soluble in alcohol and æther; it burns with a very luminous flame; its density is 0·723 at 63° F.; under a pressure of $0{\cdot}760^{mm}$, it boils at 247° F., without undergoing decomposition; the density of its vapour by calculation is 3·86=4 vols.; the average of several experiments was 3·86.

This hydrocarbon was obtained by distilling the alcohol either with sulphuric acid or with fused chloride of zinc. The action of ordinary sulphuric acid furnishes, according to the duration of the contact, either sulphocaprylic acid, $2SO^{3}$, $C^{16}\,H^{17}\,O$, HO, or a mixture of caprylene and sulphuric æther, or finally a hydrocarbon isomeric with caprylene, but possessing very different properties; its density is 0·814; it boils at about 482° F., and its boiling-point rises rapidly, its odour then becoming unbearable, resembling that of perspiration.

Sulphocaprylic acid is a colourless syrupous fluid, which is readily soluble in water and alcohol; when heated it becomes black, and is decomposed; its solution, when boiled, reproduces caprylic alcohol. It is obtained by decomposing sulphocaprylate of baryta by dilute sulphuric acid, or sulphocaprylate of lead by sulphuretted hydrogen, and evaporating the fluid *in vacuo*.

Sulphocaprylate of baryta is of a pearly-white colour, fatty, very soluble in water and alcohol, from which it is sometimes deposited in the form of acicular crystals; it is decomposed about 212° F., or by remaining too long *in vacuo*. When pressed between paper, its analysis gave numbers agreeing exactly with the formula $2SO^{3}$, $C^{16}\,H^{17}\,O$, $Ba^{2}\,O+3HO$. It is excessively bitter, but leaves a very

sweet after-taste. It serves for the formation of the other sulphocaprylates.

Sulphocaprylate of potash is white and pearly, and undergoes no change in the air; it is very soluble in water and alcohol; when heated it begins to fuse, and burns, without carbonization, with a very brilliant flame. It may be obtained by double decomposition by means of the baryta salt, or directly by saturating the acid with carbonate of potash. It is decomposed when heated above 212° F. Its constitution is $2SO^3, C^{16} H^{17} O, KO, HO$. Analysis:—

	Found.		Calculated.
SO^3, KO	34·1	33·9	33·9
Carbon.....	37·1	37·17	37·3
Hydrogen	6·92	6·93	6·9

Capryloacetic æther, $C^{16} H^{17} O, C^4 H^3 O^3$, is a liquid of a very agreeable odour, insoluble in water, and boiling at 374° F. It may be readily obtained by means of caprylic alcohol and acetic acid, with a current of muriatic acid gas, or better still by acetate of soda and sulphuric acid. The numbers obtained lead to the formula above given.

Caprylomuriatic æther is a liquid, insoluble in water and but slightly soluble in alcohol; its solution is not precipitated by silver salts; it burns with a smoky flame, which is green towards the edges. It possesses a very distinct odour of orange. Its boiling-point is about 347° F. It is prepared either directly by means of muriatic acid, or by perchloride of phosphorus. Its analysis agrees very well with the formula $C^{16} H^{17} Cl$.

Caprylohydriodic æther, $C^{16} H^{17} I$, has much analogy with the preceding. During its preparation a large quantity of red phosphorus was obtained.

By the action of sodium upon the muriatic æther, all the chlorine is removed, and the product of the action is either *capryle*, $\left\{\begin{matrix} C^{16} H^{17} \\ C^{16} H^{17} \end{matrix}\right\}$, or *caprylene*, $C^{16} H^{16}$, according as the operation has been effected by cold or heat. In the cold the sodium becomes covered with a white pellicle of chloride of sodium, which is detached by moving, and then replaced by a fresh coat, as long as the fluid retains any chlorine. Analysis:—

	Found.		Calculated.
Carbon	85·04	16	84·95
Hydrogen	14·99	17	15·04

When the action of the sodium was assisted by heat, until it was no longer attacked, a liquid possessing the odour and density of caprylene, and boiling like it at 255° F., was obtained. Its composition is $C^{16} H^{16} = 4$ vols. Analysis gave:—

	Found.		Calculated.
Carbon	85·59	16	85·71
Hydrogen	14·40	16	14·29

The density of its vapour was 3·80=4 vols. Calculation requires 3·86.—*Comptes Rendus*, May 22, 1854, p. 935.

On the Products of Distillation of Tartaric Acid. By C. Völckel.

It appears from previous experiments upon the behaviour of tartaric acid when heated, that this acid at first only loses water, and that it is decomposed at a somewhat higher temperature than that at which it fuses.

As the odour evolved by tartaric acid during decomposition resembles that given off by sugar when decomposed by heat, the author has submitted the acid to dry distillation, and found that it furnishes, although in smaller quantity, all the products obtained by the dry distillation of sugar (Chem. Gaz., vol. xi. p. 461), as well as acetic, pyroracemic and pyrotartaric acids.

The dry distillation of tartaric acid may be so managed as to produce the decomposition of almost the whole of the acid, only an inconsiderable carbonaceous residue being left. Anhydrous tartaric acid, $C^8 H^4 O^{10}$, when heated, undergoes two distinct and independent decompositions. Thus it is decomposed,—1st, into carbonic acid, oxide of carbon and acetic acid; and 2nd, into carbonic acid and pyroracemic acid, $C^6 H^4 O^6$:—

1. $C^8 H^4 O^{10} = C^4 H^4 O^4 + 2CO^2 + 2CO$.
2. $C^8 H^4 O^{10} = C^6 H^4 O^6 + 2CO^2$.

The lower the temperature, the more does the decomposition go on in accordance with the second mode. The greater part of the pyroracemic acid is driven off undecomposed, but another portion is converted into syrupous pyroracemic acid, and this is afterwards further decomposed into carbonic and pyrotartaric acids. Hence is derived the brown substance which remains when the decomposition is not completed, or the small carbonaceous residue left when it is carried to completion. In this case a simple hydrocarbon is found amongst the products of decomposition.

The author consequently regards pyrotartaric acid, $C^5 H^3 O^3$, HO, as a product of the decomposition of syrupous pyroracemic acid; it occurs only in small quantity in the products of the decomposition of tartaric acid.

In the distillation of tartaric acid with pumice-stone, as a porous body, the decomposition takes place almost entirely in the second mode; but the pyroracemic acid is further changed and decomposed, so that, according to Arppe, only 7 per cent. of the weight of the tartaric acid is obtained in this manner in the form of pyrotartaric acid. The gases evolved contain but little oxide of carbon with the carbonic acid. The distillate is at first colourless, but afterwards acquires colour and becomes opake, and a little oil collects upon the surface. If it be heated, a slightly acid yellowish fluid goes over first of all with the oil-drops. All the substances obtained by the distillation of sugar were found in this distillate.

What passes over at a higher temperature is diluted pyroracemic acid; when this is sufficiently concentrated, the residue solidifies on cooling into a crystalline mass of coloured pyroracemic acid.

A great quantity of a brown substance is produced during distil-

lation with pumice-stone; the greater part of this is carbonized, but a portion of it is soluble in alcohol and solution of potash. This reddish-brown soluble substance contains, according to a previous investigation of the author, more hydrogen than agrees with the proportion of water, H : O, and its production may be explained by the formation of formic acid from hydrates of carbon, this acid being always found, although in but small quantity, amongst the products of this distillation.

In distilling the neutral tartrates, the acid undergoes the same changes as when it is distilled with pumice-stone.

These decompositions of tartaric acid take place in the following order:—Up to 392° F. the gaseous products are carbonic acid and a small quantity of oxide of carbon. The fluid which passes over at this temperature is acid and colourless; at 428° F. a yellow strongly acid fluid passes over, accompanied by oxide of carbon and carbonic acid. Lastly, at 472° F. the distillate becomes reddish-brown, and the volumes of carbonic acid and oxide of carbon are respectively as 2 : 1.

In the rectification of the distillate the acetic acid is contained especially in the portion which passes over at 221°–238° F., the pyroracemic acid in that obtained at 266°–356° F.; from 356°–374° F. follow pyroracemic and pyrotartaric acids, and the residue left at 374° F. is completely decomposed by a higher temperature.

Pyroracemic Acid, $C^6 H^4 O^6$.—Berzelius had already obtained this acid in two forms, volatile and syrupous. The author prepared it from the acid distillate, as a perfectly volatile fluid of spec. grav. 1·288 at 64°·4 F. It has an odour like that of acetic acid, but not very strong; it boils at 329° F., and is obtained by fractional distillation. It decomposes the salts of acetic acid. If the solution of a crystallized salt be boiled for a considerable time, the salt does not afterwards crystallize again; a yellow salt is left. The same salt is obtained immediately by means of the other modification of pyroracemic acid, as stated by Berzelius (Lehrbuch, iv. p. 219).

The author investigated a lead salt of the volatile pyroracemic acid. Its analysis is as follows:—

Carbon	18·60	18·89	6 =	450·00	18·89
Hydrogen	1·69	1·64	3	37·50	1·57
Oxygen	21·04	20·87	5	500·00	20·99
Oxide of lead ..	58·67	58·60	1	1394·64	58·55

According to Berzelius, the silver salt of the same acid has the formula $C^6 H^3 O^5$, AgO. The lead salt of the amorphous acid, which was examined by the author, did not furnish consistent results; the amount of oxide of lead varied between 54·5 and 57·8 per cent. The precipitate furnished by this acid with acetate of lead is also yellowish. Some analyses agreed pretty well with the composition of pyroracemate of lead; so that when pyroracemic acid is separated from its salts, it only passes into the syrupous form, but when concentrated it becomes partially decomposed.—*Ann. der Chem. und Pharm.*, lxxxix. p. 57.

On the Preparation of Inuline. *By* C. J. Mirault.

It is very difficult to obtain inuline from the root of *Inula* in a state of purity, if the root be treated with hot water and the inuline be allowed to settle after the concentration of the fluid. It is only after repeated treatment with charcoal that it can be obtained sufficiently white, and a good deal it thus lost by absorption in the charcoal.

It may however be readily obtained pure in the following manner:—A quantity of the root is exhausted by displacement with hot water, until a strong solution is obtained, which does not require too much evaporation; this is concentrated to 10 or 12 degrees of the areometer, when double its quantity of alcohol of spec. grav. 0·860 is added to it. The inuline is thrown down in a nearly white powder, which is dissolved afresh in a small quantity of distilled water; this solution is treated with bone-black, and again precipitated with the same quantity of alcohol; the precipitate is collected on a filter and dried, which now takes place very rapidly, as the fluid contains alcohol.

Although alcohol is employed in this process, it is still a very œconomical method, as but little of the alcohol is lost.—*Journ. de Pharm. et de Chim.*, 3rd ser., xxv. p. 205.

ANALYTICAL CHEMISTRY.

On the Detection of Blood-spots. *By* J. Löwe.

For the recognition of spots of blood upon linen and other fabrics formed of non-azotized filaments, the author recommends the production of ferrocyanide of potassium from the nitrogenous animal matter. By the author's method, a fragment of the linen which has been soaked in blood is moistened with distilled water in a porcelain cup until the dried red mass is completely dissolved, and the linen appears nearly colourless. The linen is then taken with a pair of forceps, folded up, and pressed between two glass plates; it is then well washed with distilled water, the whole of which is added to the red contents of the cup. Carbonate of potash is then added to this, and the whole evaporated to dryness at a temperature of 221° F.; a higher temperature must be carefully avoided. The anhydrous residue thus obtained is put into a longish glass tube, which is drawn out into a point at the bottom; it is then covered with a layer of carbonate of potash, in order, as far as possible, to prevent the access of the air, which would readily produce a conversion of the cyanide of potassium into cyanate of potash during the fusion; the latter salt is entirely useless in the formation of ferrocyanide of potassium, so that a negative result might readily be obtained in this way. The fusion may also be effected in a small narrow iron crucible, closed, like a platinum crucible, with a tight overlapping lid.

The mass in the glass tube is exposed to a strong melting heat, assisted by the blowpipe, and allowed to cool; the tube is then cut through by a file in the neighbourhood of the dark mass, the part

containing which is thrown into a test-glass in which there is a little warm water and iron filings or sulphuret of iron. The production of ferrocyanide of potassium is facilitated by the application of a gentle heat; the solution is filtered away from the metallic residue into another test-glass, the alkaline filtrate slightly acidulated with muriatic acid in order to decompose the carbonate of potash, and 2 or 3 drops of chloride of iron are then added to it. The fluid immediately acquires a yellowish-green colour, the resulting prussian blue being suspended in consequence of its finely-divided condition in the solution, which is of a yellow colour from the excess of the iron salt. After standing a short time, the blue precipitate settles to the bottom of the tube, and may then be recognized by its characteristic properties. A great number of experiments, performed with very small pieces of linen impregnated with blood, always gave a positive result, whether the blood had been a long or short time attached to the linen; and the author is firmly convinced that this method would be applicable even after an interval of several years. Linen impregnated with sweat was fused with carbonate of potash, in order to ascertain whether the ammoniacal compounds contained in the cutaneous secretion might assist in the formation of cyanogen, which would, of course, in many cases render the experiment doubtful; but not the least traces of any blue flakes were to be seen on the addition of chloride of iron and long standing. The solution of the iron salt was repeatedly filtered before being used, in order to avoid all chance of mistake, and the tube afterwards closed with a cork. Moreover, it is more probable that ammoniacal compounds would have been decomposed and volatilized in the presence of alkalies at a lower temperature, than that the cyanogen should have been produced from the constituents of the ammonia at the high temperature required for the formation of the former substance. The great richness of the blood in proteine substances is favourable to the formation of cyanogen, even when operating upon very small quantities; and the author is of opinion that this experiment is sufficiently characteristic to prove the presence of a fluid so complicated as the blood in doubtful cases.

When the similarity of organic pigments with the colouring matter of the blood gives rise to some doubt, this may readily be removed by the well-marked behaviour of the former with ammonia, hypochlorite of lime, soda or free chlorine; and as regards rust-spots, whether upon stuffs or upon the blades of cutting instruments, they never can produce cyanide of potassium by fusion with carbonate of potash.—*Archiv der Pharm.*, lxxvii. p. 56.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Application of Murexide as a Colouring Matter for Wool.

The beautiful researches of Liebig and Wöhler upon uric acid and its derivatives made us acquainted with a peculiar substance, to which they gave the name of alloxan. This body is obtained by

adding very gradually 1 part of uric acid to 4 parts of nitric acid, of a specific gravity of from 1·45 to 1·5. The uric acid is dissolved with evolution of nitrogen and carbonic acid, accompanied by a considerable rise of temperature, which must be prevented as much as possible; on cooling, the mass becomes nearly solid, from the deposition of white granular crystals of alloxan. If these crystals be drained and dissolved in a very small quantity of water, and exposed to spontaneous evaporation in a moderately warm room, large, brilliant, colourless crystals, in the form of short right rhombic prisms, will be obtained. Alloxan is remarkable for the facility with which it undergoes changes when treated with different substances, and for the number of curious compounds thereby produced. Thus if sulphuretted hydrogen gas be passed through a solution of it, sulphur is precipitated and a new body formed, to which the name of alloxantine has been given; or if its solution be slightly acidulated and a slip of zinc placed in it, the same body will be produced under the influence of the nascent hydrogen evolved during the dissolution of the zinc. Alloxantine being sparingly soluble in cold water, readily separates in crystals, which may be obtained pure by solution in hot water, for, unlike alloxan, it is not decomposed by continued boiling. If 4 parts of alloxantine and 7 of alloxan be dissolved in 240 parts of boiling water, and 80 parts of carbonate of ammonia be added, a very peculiar body will be formed, which will crystallize on the liquor cooling. These crystals are of a beautiful garnet-red colour by transmitted light, and have a beautiful iridescent green by reflected light. To this body the name murexide was given, from the Murex or shell-fish, from which it was supposed the Tyrian purple was formerly procured. Previous however to the experiments of Liebig and Wöhler, Dr. Prout had described the same substance under the name of purpurate of ammonia but obtained in a somewhat different way. So readily is this body formed, that a solution of alloxan will stain the skin purple in consequence of its production. This fact led its second discoverers to imagine that, like the Tyrian purple, it might be employed as a dye-stuff. The difficulty however of obtaining it, and of fixing it upon the fabric when formed, prevented for that time the idea from proving fertile.

Some time since, however, Dr. Sacc turned his attention to the subject, and led by the fact above mentioned, that a solution of alloxan stained the skin, came to the conclusion, that by impregnating a piece of woollen cloth with that substance, he might be able to produce the murexide directly in the tissue. He tried the experiment, and succeeded in dyeing a piece of cloth of an amaranthus tint, far more beautiful than that produced by cochineal. He communicated the results of his first experiments, still incomplete, to M. Albert Schlumberger, who has succeeded, by modifying and completing the experiments of Dr. Sacc, in rendering the process, merely indicated by the latter, perfectly practicable.

His process is simple enough. He prepares a solution of alloxan, formed of 30 grms. of alloxan to each litre of water, and soaks the tissue to be dyed in it, the excess of liquid being then squeezed out

in the ordinary way, or by pressure between rollers. The cloth is then dried at a gentle temperature, and after an ageing of twenty-four hours the colour is brought out by passing the cloth over a roller heated to 212° F. For this purpose the drying machines composed of several drums would answer perfectly, the cloth being successively passed over each, the greatest care being taken to avoid folds; woollen yarn and wool should be put in a stove heated by steam. According as the heat is communicated to the cloth, a magnificent purple tint, far more beautiful than anything hitherto produced by the ammoniacal preparation of cochineal, or by red dye-woods, makes its appearance as if by magic. The intensity varies according to the strength of the solution of alloxan which has been employed. It is only necessary to wash the cloth in cold water to give to the shade its full brilliancy.

M. Sacc found that the finest and most vivid shades could only be communicated to the tissues mordanted with salts of peroxide of tin, and M. Schlumberger has confirmed this observation. Cloth not mordanted did not give very satisfactory results, even after a prolonged exposure to warm and damp air. He obtained the most satisfactory results by soaking the cloth in a solution composed of equal parts of perchloride of tin and oxalic acid, of a specific gravity of 1·006. In this solution, at a temperature of about 100° F., the cloth is to be allowed to remain for an hour, then rinsed and dried, and is then fit to be treated with alloxan. If stronger solutions of the mordant be employed, there is a considerable loss of colouring material, and a deterioration of the shade. This may be attributed to the presence of too great an excess of stannic acid, which from its opacity may mask the murexide, or by its acid reaction may decompose it. This is especially the case if chloride of tin be employed instead of stannate of soda. Experience has shown that fabrics freshly mordanted give better results than those which have been mordanted for some time; the depreciation in purity and brilliancy of tint in the latter may even amount to 20 or 30 per cent.

Murexide, as we have already remarked, being produced by the action of heat and ammonia, it occurred to M. Daniel Dollfus, and the other members of the committee for the chemical arts, appointed by the Société Industrielle of Mulhouse, to report upon the memoirs of M. Schlumberger, to try the effect of exposing a piece of cloth, treated with alloxan, to the vapours of ammonia. The result confirmed their anticipations, for the colour was immediately produced without the necessity of ageing the cloth after its impregnation with the alloxan. There can therefore be no doubt that the best results will be obtained in future by the employment of ammoniacal vapours, for, besides the saving of time, there will also be a saving of alloxan. This substance is very liable to decompose, especially in the presence of even minute traces of reducing agents, such as protochloride of tin or sulphurous acid; traces of the latter substance always remain in the cloth after the operation of bleaching, no matter how well washed it may be, and would be quite sufficient to prevent the formation of the murexide.

As yet all the attempts that have been made to communicate the murexide-purple to cotton or silk have failed, that substance having an affinity apparently only for wool, to which it gives a very durable and permanent dye. Sun-light, so destructive to other purples, appears to have but little action upon that of the murexide; a piece of cloth dyed of a rose colour had its tint scarcely altered by exposure to the full action of the strongest sunshine during two days, and the colour was only fully discharged by an exposure of more than two months. Boiling water and steam completely destroy the colour produced upon cloth mordanted with salts of tin; the decoloration commences in boiling water at a temperature of about 153° F., and augments with the increase of temperature. This destruction of the dye is caused by the action of the mordant, for cloth dyed without the use of a mordant not only supports to a certain extent the action of boiling water, but even acquires a uniform, and perhaps a more beautiful and deeper tint than that given by prepared woollen fabrics. Further experience may show that hot water and the application of ammonia alone may be advantageously substituted for the mordanting and the passage over heated cylinders.

Cold alcohol or æther have no action upon murexide-purple; the former liquid destroys it at boiling temperature, without being coloured purple as water is. Alkalies, especially in a caustic state, are very destructive to it; if a piece of cloth dyed with murexide be dipped into a solution of caustic soda, it assumes a violet-blue colour, and is then decolorized. Soap, acting as a weak alkali, after a time alters it. Chlorine has no immediate action upon it, at least not in weak solutions. Acetic and oxalic acids are not sufficiently energetic to immediately discharge the colour. Hydrochloric, nitric, and sulphuric acids act as decolorizers; nevertheless the latter acts less quickly than the first two, and, what is singular, the colour almost destroyed by sulphuric acid reassumes a rose-violet by immersing the tissue in ammonia.

Bichromate of potash, chlorate of potash, acetate of lead, acetate of alumina, are without action upon murexide. This is not the case however with reducing compounds, such as protochloride of tin, sulphuret of ammonium, protosulphate of iron, which destroy the rose tint very rapidly; the protochloride of tin produces a blue tint before it decolorizes it. The reduction of the murexide gives birth to a new substance, which in its turn may reproduce that substance by a properly conducted oxidation.

From these reactions it is evident that the rose, amaranthus, and purple shades produced with the murexide, and which exceed those produced by all other means in richness and brilliancy of tints, have also the advantage of being the most solid and durable, an advantage which will no doubt be soon appreciated.

We have now to speak of the sources from whence the supply of uric acid may be obtained, should the employment of murexide become general. At present the price of that substance, which has never hitherto become an article of commerce, would be so high that the murexide-purple would be far more expensive than that

produced with cochineal; but if we recollect, that, independent of the excrements of serpents, from which hitherto uric acid has been made, those of pigeons, and especially of all carnivorous birds, silk-worms, &c., and above all Peruvian guano, which may be obtained in immense quantities, are very rich in uric acid, and it may be produced from them at a very moderate price as soon as it becomes an article of commerce. No doubt, if necessary, fowl might be so fed as to produce it in much larger quantities than they do naturally.

Connected with this part of the subject, we may mention, that in the making of the alloxan from the uric acid, a considerable quantity of the former remains in the acid mother-liquid, from which the crystals of alloxan separate. This portion could not be used to impregnate tissues, in consequence of the nitric acid present, and would cause a considerable loss of material, and a considerable enhancement of the cost of the dye, unless it could be utilized. If a piece of zinc be introduced into the acid mother-liquid, alloxantine will be formed, which may be recovered by evaporating the liquid and allowing it to separate out. This substance, as we have before remarked, will also produce the purple colour, and a mixture of it with alloxan will afford the best conditions for its production.

M. Schlumberger has indulged in some curious speculations relative to the existence of this colouring matter ready formed in nature, which it may be interesting to notice. M. Sacc has found that poultry, and especially birds with very brilliant plumage, such as the different parroquets, do not produce sensible traces of uric acid during their period of moulting, whilst the quantity is very large when their feathers are fully developed. The question naturally suggests itself, what becomes of the uric acid in the former case? May it not be transformed by some as yet unknown metamorphosis in the animal body into a substance like alloxan, capable of colouring the feathers? Murexide, as we have observed, is green by reflected light; a substance then which gives violet (red and blue) and green (yellow and blue) can undoubtedly produce all shades of colours, which are made up of those three colours. How curious if it should hereafter be found that murexide was indeed the source of all the varied hues of birds' plumage! Still further, it is chiefly those animals which have but one means of exit for their excrements, and who produce large quantities of uric acid, that exhibit a display of colouring. Thus, for example, we have the skin of the serpent and lizard, the scales of fish, the wings of butterflies, often coloured in the most gorgeous manner, whilst the skins of the mammalia are dull, and without that iridescence and metallic lustre which is so characteristic of the colouring of some of the classes of animals mentioned. These are however mere speculations, but they nevertheless lead to a very unexpected supposition. The ancients were acquainted with a process for dyeing wool of a fine purple, which has been lost to our days, or at least is only practised in the East. Tradition however tells us that this beautiful purple tint was produced by pounding a quantity of small shell-fish, and adding to the mass either a quantity of urine in the state of putrefaction, or water

in which some of the same shell-fish had been allowed to putrefy. The cloth soaked in the liquid produced by these mixtures only developed the beautiful purple colour after long exposure to the air, and probably to heat. This mode of producing the colour so strikingly resembles that by which the new colour of murexide is produced, that one is tempted to believe that the Tyrian purple was produced by that substance; and that many centuries before the beautiful discovery of Liebig and Wöhler, murexide was formed by the action of ammonia in the putrid matter employed upon substances derived from the uric acid which must exist in the intestines of the shell-fish pounded up.—*Bulletin de la Société Industrielle de Mulhouse*, No. 123, p. 242; and *Dublin Journ. of Indust. Progress*, June, p. 173.

On the Use of Wood-gas for Illumination in Heilbronn. *By* Dr. H. Fehling.

The old city of Heilbronn is the first German town which has been lighted with wood-gas. The novelty of this method of illumination will render it interesting to many to know whether the wood-gas has been found to answer in this experiment. It is natural that every new invention should be received with distrust, and sometimes meet with opposition. Narrow minds, or such as feared an interference with private interests from the introduction of wood-gas, have advanced many objections, which have been already partially contradicted by the experience of nearly two years in Munich. It was particularly and repeatedly asserted that wood-gas could not be conveyed without suffering loss in its illuminating power. This statement, which every one versed in such matters knew to be groundless, has now been completely disproved in Heilbronn, as not only the town, but also the railway station situated at some distance, are lighted with wood-gas.

The manufactory of wood-gas in this place has been under the direction of G. Schäufelen from the 1st of December, and since that date the town has been lighted with wood-gas. During the first few days the opponents of the scheme were gratified, for the gas gave a bad light; but, on examination, it was found that the fault lay with the purifiers, which had not been worked carefully, the gas, instead of passing slowly through the milk of lime, having been allowed to flow without any impediment over the surface of the liquid, so that it arrived at the gasometers without any purification, and contaminated with 20 per cent. of carbonic acid. By improving the purifying apparatus, however, the carbonic acid was completely got rid of, and a gas obtained equal in every respect to that prepared from the best coal.

This result was arrived at by a series of experiments made in Heilbronn on the 7th and 8th of January. From these it appears that wood-gas gives a sufficiently clear light, that the quantity of gas consumed is not in too great a proportion to the light furnished, and that the strength of the light is not diminished by its conveyance to distant localities. That the strength of the light is sufficient was

shown by a comparison with coal-gas; the light given by the employment of $4\frac{1}{2}$ cub. feet per hour of gas prepared from the best Saar coal, is stated to equal that of 12 to 14 candles; Frankland found the light with 5 cub. feet per hour of gas from the best Newcastle coal = 14·5 sperm-candles, but this gas is far better than that from the Saar coal. According to the contracts of the gas companies in Stuttgart, Heilbronn, and probably in many other towns, the gas in the street-lamps (at $4\frac{1}{2}$ cub. feet per hour) furnishes at least the light of 7 wax-candles; the experiments with something less than $4\frac{1}{2}$ cub. feet of wood-gas per hour gave a light equal to $13\frac{1}{5}$ candles, and consequently nearly double the last-mentioned. With 5 cub. feet a street-burner gave the light of 16, and a Dumas' Argand burner of 24 candles. According to measurements made in Munich and Ulm with coal-gas, its light, with a consumption of $4\frac{1}{2}$ cub. feet per hour, varied between that of 8 and 10 stearine candles, six to the pound. Thus it appears that the consumption of wood-gas need not be greater than that of coal-gas.

The author adds, that in the Falcon hotel, 9 lights consumed 30 cub. feet of gas per hour, or $3\frac{1}{3}$ cub. feet per hour for each burner, which is certainly not much.—*Gewerbebl. für das Grossherz. Hessen.*

On the Preparation of Fuming Nitric Acid.
By Prof. C. Brunner.

A mixture of 100 parts of crystallized nitrate of potash and 5 parts of flowers of sulphur is put into a retort, and 100 parts of English sulphuric acid are poured over it. With large quantities, the best plan is to add the acid in fractions, as the mixture becomes considerably heated. It is now distilled with a gentle heat into a well-cooled receiver, when a fuming acid of a strong red colour passes over from the commencement. After a time the sulphur separates from the mixture, and floats on the fluid with a pure yellow colour. From this time little more fuming nitric acid passes over, its place being taken by the ordinary acid. It is therefore advisable to change the receiver. If about 50 parts of the above-mentioned mixture have gone over, this is about the right proportion.

The acid thus obtained is very strongly fuming, and of a red colour. It contains a considerable portion of sulphuric acid, as may be shown by its reaction with chloride of barium. If it be again distilled by itself with a gentle heat in a retort furnished with a long tube attached, without luting, to the neck of the retort, a very strongly fuming acid, quite free from sulphuric acid, passes over; this separates into two strata, of which the upper is the fluid substance which was regarded by Berzelius as nitrate of oxide of nitrogen, by others as hyponitrous acid, but which is universally considered to be the fuming principle of the ordinary fuming nitric acid. It is remarkably volatile, and cannot well be preserved at ordinary temperatures, but may be made use of to mix with the ordinary nitric acid, so as to convert it into fuming acid.—*Mittheilungen der Naturf. Gesellsch. in Bern.*

THE CHEMICAL GAZETTE.

No. CCLXXXI.—July 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Metals associated with Platinum. *By* E. Fremy.

Previous researches had shown me that the platinum residues possess a variable composition, and furnish uncertain products on analysis. Moreover, all chemists are aware that the metals which are associated with platinum are difficult to prepare, and that the characters of their solutions are not constant; thus M. Claus* has proved within the last few years that the salts of iridium always contain a certain quantity of ruthenium, and I have myself had occasion to observe that the properties of the salts of rhodium often differ from those described by Berzelius.

I therefore thought that, in the investigation I was undertaking, the first point of importance was to analyse exactly the different residues of the ores of platinum, and then to find a ready and certain method of preparing the different metals which are found mixed with platinum. It appears from my analyses that the residues of platinum may be divided into three classes, according to their composition:—

1. *The pulverulent residue* is a mixture of iridium and rhodium; it is obtained from acid solutions precipitated by iron, and only retains a small quantity of osmium; the metals forming this residue dissolved in the nitromuriatic acid by the aid of the bichloride of platinum.

2. *The residue in scales*, which is known to all chemists by the improper name of *osmide of iridium*, is a quaternary alloy of iridium, ruthenium, osmium and rhodium; the rhodium is present in but small quantity.

3. *The granular residue* consists essentially of rhodium, osmium and iridium.

Thus to obtain rhodium, the pulverulent and granular residues must be operated on; all three kinds of residue may be employed in the preparation of iridium; the scaly residue alone furnishes ruthenium; and osmium must be prepared principally from the scaly and granular residues.

These analytical results being established, I now proceed to the method which I make use of in operating upon these residues; it differs completely from that which I described in a previous memoir, and is founded partly upon the great fixity of the oxide of ruthenium,

* Chem. Gaz. vol. iv. p. 437.

and partly upon the striking analogies which osmium presents to arsenic. I will take the residue in scales as an example.

Oxide of ruthenium being capable of bearing exposure to a red heat without decomposition, and osmium undergoing an actual roasting by the action of oxygen, and furnishing a volatile acid like sulphur and arsenic, I thought that the residue might be roasted, so as to decompose it like the metallic sulphurets and arseniurets; and experiments have not only confirmed this supposition most completely, but have also given an interesting result, to which I had not looked forward; for by roasting the residue, I obtained not only osmic acid of great purity and in large quantity, but also oxide of ruthenium in well-defined crystals, a form under which it has not hitherto been known.

I now proceed to describe an apparatus which has been in action for a long time in my laboratory, and which being now set up in the workshops of MM. Démontis and Chapuis, will furnish chemists with products which have hitherto been but little known, but which cannot fail of receiving some interesting applications.

I long thought the residue of the platinum ore could not be roasted easily except in a current of oxygen; but I now perform the roasting by means of atmospheric air, which is deprived of any organic bodies contained in it by traversing a tube filled with pumice-stone and sulphuric acid. The residue is heated to redness, and placed in an earthen or platinum tube; the latter is best; the air is drawn into the apparatus by means of an ordinary water-aspirator; the tube is in communication with a series of glass flasks, in which the osmic acid condenses, and it is also furnished, at the part which projects from the furnace, and through which it communicates with the flasks, with a few fragments of porcelain, which become covered during the operation with beautiful crystals of oxide of ruthenium, which, although not volatile, is carried off by the vapour of osmic acid. The air which has traversed the flasks, and which is still saturated with vapour of osmic acid, passes into a solution of potash, and finally to the aspirator; the osmiate of potash thus produced is treated with a few drops of alcohol, and collected in the form of crystallized osmite of potash, which is insoluble in water containing alcohol.

This roasting consequently is not attended with any difficulty, and furnishes the following products:—1st, very pure osmic acid, often in a proportion of more than 40 per cent. to the quantity of residue employed; 2nd, osmite of potash, from which metallic osmium and its derivatives are easily prepared by a process described by me in a preceding memoir; 3rd, crystallized oxide of ruthenium; 4th, an alloy of iridium and rhodium, which remains in the roasting tube.

The operation just described is not only important for the preparation of bodies, such as osmic acid and oxide of ruthenium, which have hitherto only been obtained with difficulty, but also serves in some degree to complete the history of osmium, by showing that this body differs completely in all its properties from the other

metals associated with platinum, and that it appears actually to play the same part in the ore that is performed by arsenic in the metallic arseniurets.

We may now assume that osmium will combine with hydrogen, and that, like arsenic and phosphorus, it may enter into organic combinations, and produce some of those interesting compounds which have lately been discovered. I have undertaken some researches upon this subject, which I shall hereafter submit to the Academy, merely stating that I have ascertained the existence of a more highly oxygenized acid than osmic acid, produced by submitting osmiates to the action of oxygen and of oxidizing agents. If this acid is represented, as some analyses lead me to believe, by the formula OsO^5, the series of oxides of osmium will be

$$OsO,\ Os^2O^3,\ OsO^2,\ OsO^3,\ OsO^4,\ OsO^5,$$

and will present remarkable analogies with those of nitrogen, phosphorus and arsenic. The new acid is not very stable, and forms with potash and soda salts of a dark brown colour, which crystallize in alkaline solutions.

The alloy of iridium and rhodium left after the roasting of the residue is often mixed with oxide of ruthenium, which has not been carried off by the vapour of osmic acid, and also retains traces of osmium. I first extract the oxide of ruthenium by fusing the residue with potash, which dissolves the metallic oxide, and then separate the iridium from the rhodium by the following method, which differs but little from that previously discovered by M. Wöhler.

The alloy is heated with 4 parts of nitrate of potash, and the mass treated with boiling water, which often furnishes on cooling fine octahedric crystals of osmite of potash; the residue is treated with nitromuriatic acid, which converts the iridium into chloride; this substance afterwards combines with chloride of potassium, forming a double salt soluble in boiling water, and crystallizing on the cooling of the solution; the insoluble residue is mixed with chloride of sodium, and treated at a dull red heat with a current of dry chlorine; in this manner a double chloride of sodium and rhodium is formed, which is soluble in water, and crystallizes from its solutions in violet octahedra, often of considerable size.

This easy mode of preparing the salts of rhodium, by the process just described, will enable us to complete the study of this metal, which deserves the attention of chemists from its insolubility in nitromuriatic acid, its metallic lustre, which approaches that of silver, the beauty of its crystalline combinations, and especially its analogies with platinum and iridium.

I have already ascertained that the salts of rhodium, when submitted to the action of ammonia, give rise to a class of ammoniaco-rhodical salts, in which the quaternary base, containing the elements of ammonia and oxide of rhodium, forms readily crystallizable salts with the different acids; these correspond with the salts formed by platinum, palladium and iridium, under the same circumstances.—*Comptes Rendus*, June 5, 1854, p. 1008.

On some Homologues of Quinoïle and its Derivatives.

By A. Lallemand.

The stearoptene of the essential oil of thyme, or thymole, the properties and composition of which I recently made known, gives rise, under the influence of oxidizing agents, such as chromic acid or a mixture of sulphuric acid and deutoxide of manganese, to a solid crystalline substance, which is related by its properties and metamorphoses to the quinoïle or quinone obtained by Wöhler in oxidizing kinic acid.

To prepare this compound, which I shall call *thymoïle*, the most simple process consists in combining thymole with an excess of sulphuric acid. The sulphothymic acid, diluted with from five to six times its bulk of water, is introduced into a retort, and mixed with an excess of deutoxide of manganese; the mixture becomes very much heated, and distillation commences; on assisting it with a moderate heat, an aqueous liquid passes into the receiver, mixed with oily drops of an orange-yellow colour, which soon solidify. The fluid portion is dilute formic acid. There remains in the retort a solid brownish resin, which dissolves in water, imparting to it a red colour. The solid matter condensed in the receiver is dissolved in hot alcohol, or rather in a mixture of alcohol and æther, from which it soon crystallizes.

Thymoïle has a very strong aromatic odour, slightly resembling that of iodine; it is very sparingly soluble in water, more readily in alcohol, but most readily in æther, by long contact with which however it is altered. It crystallizes in brilliant square prisms, of a beautiful orange colour. It melts at 118° F. into a dark yellow liquid, and diffuses copious fumes at 212°; but on attempting to distil it, the temperature rises rapidly to 455° F., and it is partly decomposed into a dark red oily residue, which congeals into a solid mass, of a beautiful violet tint with an iridescent reflexion; at the same time a great portion sublimes without alteration, and collects in the neck of the retort.

Three concordant analyses gave for its formula $C^{24} H^{16} O^4$, homologous with $C^{12} H^4 O^4$, which represents quinoïle, the physical properties and characteristic reactions of which it possesses. If, in fact, it be submitted to the action of reducing agents, placed in contact, for instance, with sulphurous acid, it soon assumes a deep violet tint, and after some days becomes converted into a white crystalline substance, sparingly soluble in water, but very soluble in alcohol and æther. It dissolves largely in cold fuming nitric and concentrated sulphuric acids, from which water again precipitates it unaltered. After the lapse of some time, or at an elevated temperature, these acids convert it into new products. The action of chlorine is also very slow, and requires the assistance of heat, when it furnishes chlorinated products of the same formula; solution of ammonia dissolves it, gradually acquiring a blackish-red tint; the fixed alkalies act in the same manner.

The final product to which sulphurous acid gives rise is homolo-

gous with the pyroquinole, or colourless hydroquinone of Wöhler; it crystallizes from weak alcohol on cooling in small, colourless, quadratic prisms. Its analysis, after desiccation *in vacuo*, led to the formula $C^{24} H^{18} O^4$. Its action on thymoïle resembles that of hydroquinone on quinoïle; on mixing equal weights of the two substances dissolved in boiling alcohol, a beautiful phænomenon of crystallization occurs; the mixture instantly turns deep red, and on cooling deposits beautiful prismatic crystals, of a violet colour by transmitted light, and metallic bronze by reflected, similar to that observed on the elytra of many Coleoptera. The dilute formic acid, which distils over in large proportion in the preparation of thymoïle, likewise reduces it, and converts it into these two new products.

Colourless *thymoïlole*, submitted to the action of oxidizing agents, reproduces the two successive terms from which it was formed. Perchloride of iron, dilute nitric acid, chlorine water, instantly cause the formation of violet crystals, and a larger quantity of the reagent reproduces thymoïle. The new compounds which I have described lead me to regard quinone and its derivatives as the first terms of several series characterized by peculiar chemical and physical properties. We have, in fact,—

$C^{12} H^4 O^4$, quinoïle (quinone), the homologue of $C^{24} H^{16} O$, thymoïle.
$C^{12} H^5 O^4$, quineide (green hydroquinone) ..... $C^{24} H^{17} O^4$, thymeide.
$C^{12} H^6 O^4$, quinoinole (pyroquinole) ..... $C^{24} H^{18} O^4$, thymoilole.

Between the two terms of these three series five others may be intercalated, the production of which is very probable. Chemists adopt for quinoïle an equivalent double that of the preceding; but the existence of thymoïle and its volatility appear to me to justify the halving of it, and, as far as I am aware, no reaction, no metamorphosis requires the employment of so high an equivalent. The three compounds which I have described experience numerous decompositions, which I have partly examined; but my investigation is not sufficiently advanced for publication.—*Comptes Rendus*, June 5, 1854.

On the Oil of Pulegium micranthum. *By* A. Buttlerow.

Pulegium micranthum grows abundantly on the southern steppes of Russia, especially round Sarepta and Astrachan. The author has investigated a sample of the essential oil of this plant, prepared by M. Becker of Sarepta.

This oil has nearly the composition of camphor, $C^{10} H^8 O$. It is a thin fluid, holding an intermediate place in regard to taste and smell between the oils of *Mentha piperata* and *crispa*, with a distant resemblance to oil of sage. When long exposed to a temperature of $+1°$ F., it undergoes no change, and does not deposit any stearoptene. It readily absorbs oxygen from the air, becoming in course of time thicker and of a yellowish-brown colour.

The crude oil was purified by distillation; it began to boil at 396° F., then quickly rose to 441° F., and remained stationary at

this temperature until the completion of the distillation, which went on very rapidly. There was only a slight resinous residue. The rectified oil is nearly colourless, with only a slight trace of yellow; it has the taste and smell of the crude oil, and dissolves very readily in alcohol, æther and oils; at 63° F. it has the spec. grav. 0·932. If the oil be left for some time in contact with oxygen over mercury in a glass tube, it absorbs the oxygen without any formation of carbonic acid, and thus acquires a higher specific gravity. It absorbs muriatic acid gas pretty readily, acquiring a brown colour, but furnishing no crystalline compound when cold; the muriatic acid is but weakly combined, as the greater portion of it may be removed by washing with water. Analysis:—

Carbon	78·45	78·16	10	78·94
Hydrogen	10·63	10·69	8	10·53
Oxygen	10·92	11·15	1	10·53

Oxidizing bodies, such as nitric acid, chromic acid, &c., all give rise to the same products. The oil always furnishes acetic acid and other acids of the series $(C^2 H^2)^n + O^4$, among which propionic acid is present.

Solution of potash converts the oil into a brown resin. If the experiment be made in a retort, an acid fluid distils over at the same time; this contains an acid of the series $C^n H^n + O^4$, and also an altered oil, which possesses a different odour from that of the original oil, and is less easily acted upon by potash. The resin is amorphous, with an acid reaction; it is insoluble in water, but soluble in alkalies and alcohol. It is precipitated by acids from its alkaline solutions. At ordinary temperatures it is brittle and pulverizable. Its analysis gave,—

Carbon.....	77·96
Hydrogen	3·59
Oxygen	13·15

These numbers indicate that this resin is produced from the *Ol. Pulegii* by the action of the potash, exactly as the other resins result from their corresponding oils by the abstraction of hydrogen and higher oxidation. The author does not venture to propose a formula for this resin from the above analysis, as he obtained it in too small a quantity to determine its capacity of saturation, and to make sure that he was operating upon a pure substance.

If the oil be dropped slowly into fusing hydrate of potash, the mass rapidly acquires a brown colour, from the formation of a similar resin to that produced by the action of solution of potash upon the oil. The mass dissolves in water with a brown colour; and when supersaturated with acids, the resin is separated, whilst the solution acquires an odour of creosote or castoreum. If it be then distilled, an acid fluid is obtained, which contains several acids of the series $C^n H^n + O^4$, especially acetic and valerianic acids. If the acid fluid be saturated with soda, and precipitated in fractions with nitrate of silver, salts of various composition are obtained; the first precipitates corresponded with acetate of silver, the latter furnished a quantity of

silver agreeing with a valerianate. Others lay between the two salts just mentioned. It is therefore extremely probable that various acids, from acetic acid to valerianic acid, are formed by this process of oxidation.

By the distillation of the oil with chloride of lime and water, the author obtained a small quantity of a substance which he believed to be chloroform. This oil would therefore behave like those from which Chautard stated that he obtained chloroform.—*Bull. de St. Pétersb., Cl. Phys.-math.*, xii. p. 241.

On Molybdate of Soda. By Dr. F. E. Zencker.

When caustic soda is added to a solution of crystallized molybdate of soda, and the whole is concentrated by evaporation, scales of a pearly lustre are deposited, which are very soluble in water. They contained 30·70 per cent. of soda, and are consequently the neutral anhydrous salt, which ought to contain 30·97 per cent. of soda.

If nitric acid be added to the solution of molybdic acid in carbonate of soda or caustic soda as long as the resulting precipitate is again dissolved, and no longer than till the fluid has an acid reaction, large colourless crystals are obtained, which are often an inch in length, and belong to the monoclinohedric system. Analysis gave 24·97 water 11·87 soda and 63·16 molybdic acid, agreeing with the formula $4NaO+9MoO^3+28HO$, which, with the exception of the amount of water, corresponds with the potash salt of Svanberg and Struve, $4KO+9MoO^3+6HO$. At 212° F. the salt lost 23·33 per cent. of water; the salt, dried at 212° F., has therefore the composition $4NaO+9MoO^3+2HO$.—*Journ. für Prakt. Chem.*, lviii. p. 486.

On the Deliquescence and Efflorescence of Salts. By P. Kremers.

In the deliquescent salts three different states may be observed without exception within certain temperatures,—at a certain low temperature the salt deliquesces; at a higher one, the condition of neutrality or stability; and lastly, at a higher temperature still, and when the salt contains combined water, it effloresces. But whilst this succession of states appears to be the same in all salts, the position and extent of the intermediate state are very different, so that under the same external conditions one salt is deliquescent, whilst another still remains unchanged.

It appears, from the author's comparisons of salts, that as a general rule salts with a high atomic weight, and with strong acids, are especially deliquescent. The author wishes to show by the following table, how the temperature of the state of neutrality of salts is raised in accordance with the strength of the acid, and frequently by its high atomic weight, and, on the contrary, sometimes by the low atomic weight of the base; whilst it sinks to the ordinary temperature of the atmosphere, and even lower, when these bases are replaced by others of higher atomic weight. The following table therefore

shows that the position of the neutral state of the salts varies with the position of the zero-point. With regard to this table, the author states that the three last lines give a result which contradicts what has been said above, as in these the acids with the lowest atomic weights raise the state of neutrality to the highest point, and especially as the same behaviour was also manifested previously in the investigation of the zero-point of the salts. In determining the strength of these and similar acids, the proportion which the negative constituents exhibit to the positive ones must consequently also be taken into consideration.

The extent of the neutral state is very various. In the table the *minus* sign=deliquescent, the *plus* sign=efflorescent, the 0=neutral, and the numbers indicate the number of equivalents of water.

Cl..... −Li+4 | 0Na | 0K
Cl..... −Mg+6 | −Ca+6 | $\overline{0}$Sr+6 | 0Ba+2
Cl..... −Mn | −Fe | −Co | −Ni | −Cu | −Zn | 0Hg | 0Pb | 0Ag
Br ..... −Mg+6 | −Ca+? | 0Sr+6 | 0Ba+2
Br ..... −Mn | −Co | −Ni | −Cu | −Zn | 0Hg | 0Pb | 0Ag
I ..... −Li+6 −$\overset{0}{+}$Na+4 | $\overline{0}$K
I ..... −Mg? | −Ca?
I ..... −Mn | −Ni | −Zn | 0Hg | 0Pb | 0Ag
SO^3 ..... −MgO | 0CaO | 0SrO | 0BaO
SO^3 ..... −MnO | −FeO | −CoO | −NiO | −CuO | −ZnO | 0PbO | 0AgO
NO^5 ..... −LiO | $\overline{0}$NaO | 0KO
NO^5 ..... −MgO+6 | −CaO+4 | 0SrO | 0BaO
NO^5 ..... −MnO+6 | $\overline{0}$CoO+6 | $\overset{0}{+}$NiO+6 | −ZnO+6 | −CdO+4 | 0PbO | 0AgO
S^2O^5 ..... −LiO+2 | 0NaO+2 | 0KO
S^2O^5 ..... 0MgO+6 | 0CaO+4 | 0SrO+4 | +BaO+4
ClO^5 ..... −NaO | 0KO
NaO ..... $-ClO^7$ | $0IO^7$
SrO ..... $-ClO^5+1$ | $0BrO^5+1$
CuO ..... $-ClO^5+2$ | $0BrO^5+1$

Poggendorff's *Annalen*, xci. p. 283.

On Anisamic Acid. *By* Dr. N. Zinin.

The author has obtained a new acid from nitranisic acid, formed exactly in the same manner as benzamic acid from nitrobenzoic acid.

Laurent has described two very similar nitranisic acids. That upon which the author operated was previously determined by the analysis of the silver salt; this contained exactly the quantity of silver corresponding to the formula $C^{16}H^6NO^4O^6$, Ag; it was consequently pure.

Alcoholic ammonia was poured over this acid, and the whole was

treated with sulphuretted hydrogen. Separation of sulphur took place, and a new acid was formed. After getting rid of the alcohol by evaporation and filtering the fluid, the watery solution of the ammoniacal salt of this acid remained; from this the acid could be separated, by the addition of a stronger acid, such as acetic acid, when it was deposited in long acicular brown crystals. These were deprived of colour by animal charcoal. The

Anisamic acid, $C^{16} H^9 NO^6 = C^{16} (H^7 NH^2) O^6$, thus prepared, forms thin four-sided prisms, of an inch in length and very lustrous, which become iridescent, especially whilst forming in the fluid. They are difficult of solution in water, 1 part requiring nearly 800 of boiling water for its solution, and three-fourths of the acid dissolved separate again on cooling; the remaining solution however still has a distinct acid reaction, and a sweetish acid, unpleasant taste. The acid is difficult of solution in æther, but dissolves readily in alcohol; from its hot alcoholic solution it crystallizes in shorter, but thicker, four-sided prisms, with octahedric apical faces, which are usually wanting in the longer prisms formed in the watery solution. The acid crystallizes from boiling acetic acid unchanged, as well as from tolerably strong muriatic acid, although in the latter case the needles are thinner. Hot dilute nitric acid dissolves the crystals at first without noticeable change, but when the boiling is continued, the solution becomes red, and no longer furnishes acicular crystals on cooling, but instead a mixture of brown flakes with a nearly white pulverulent body. When heated to 284° F., the crystals of anisamic acid undergo no change, and lose nothing in weight; at 356° F. they fuse into a colourless or slightly yellowish fluid, which on cooling solidifies into a crystalline mass. When further heated, the fused mass acquires a light brown colour; but if the heat be raised very carefully, a nearly colourless fluid, which solidifies very readily, passes over into the receiver, whilst nothing remains in the retort but a small quantity of charcoal; the distillate is no longer anisamic acid. When cautiously heated upon platinum foil, the acid is volatilized without residue, but with formation of copious white fumes, possessing a faint and but slightly characteristic odour, which bears but a distant resemblance to that of anisylous acid.

The watery solution of the acid produces no precipitate with solutions of lime, baryta or silver. The acid is very soluble in ammonia, the odour of the alkali being lost, and the fluid having a neutral reaction; the ammoniacal salt formed crystallizes with difficulty, but the spontaneous evaporation of its concentrated solution causes the formation of square prisms; its solution produces with salts of silver a caseous, white precipitate, which dissolves readily in ammonia and acids, but is insoluble in water. This precipitate moreover cannot be boiled with the fluid, as it then becomes brown; it may be washed and dried at ordinary temperatures, and may then be heated in the dark to 248° F. without losing its white colour or undergoing any change. When more strongly heated, this silver salt fuses, becomes black, and evolves copious fumes; the residue of silver contains carbon, which cannot readily be burnt out.

With a solution of sulphate of copper and ammonia, the acid furnishes at the ordinary temperature a small quantity of a pale blue flocculent precipitate, which increases by slight heating; the colour of the ammoniacal copper solution does not however disappear, even when the acid is added in excess. When strongly boiled, the precipitate acquires a cinnamon-brown colour, and becomes pulverulent; the supernatant fluid, when a sufficient quantity of the acid has been added, usually acquires a violet-red colour, and furnishes, on a fresh addition of the copper salt, a greenish precipitate, which does not so readily become brown by boiling; the fluid loses its colour.

Salts of lead and cadmium, when added to the ammoniacal salt of the acid, furnish white pulverulent precipitates, which are insoluble in water.

In the analysis of the acid, the determination of the carbon and hydrogen was effected by the method described by Fritzsche in his memoir on the alkaloids of *Harmala*. Analysis gave:—

Carbon	57·71	57·52	16 =	96	57·48
Hydrogen	5·45	5·58	9	9	5·39
Nitrogen	8·71	8·71	1	14	8·38
Oxygen	28·13	28·19	6	48	28·75

The silver salt of this acid, $C^{16} H^{8} NO^{6} Ag$, dried at 248° F., gave 39·10 and 39·40 per cent. of silver (calculated, 39·41).—*Bull. de St. Pétersb., Cl. Phys.-math.*, xii. p. 236.

ANALYTICAL CHEMISTRY.

On a Method of Volumetric Analysis of general application. By D. Aug. Streng.

Two courses may be followed in analytical chemistry, in ascertaining the proportionate quantities of the constituents of a compound,—the individual constituents of the substance under examination may be separated and obtained in a solid form, and then weighed, which generally requires very complicated operations; or a shorter way may be taken, by producing a reaction upon the body under investigation by means of a reagent of known strength, the conclusion of which is recognized, according to the different methods, by a great number of characters; the quantity of the body to be determined is then calculated from that of the reagent employed. These two methods are denominated respectively analysis by weight and analysis by volume; and both are equally capable of furnishing perfectly correct results. Nevertheless chemists have hitherto confined themselves almost entirely to the employment of the former method, whilst the volumetric method has been resigned to the manufacturers, and even they have only partially availed themselves of it. It is only quite recently that the most distinguished chemists have paid any attention to this latter branch of analytical chemistry; but the last few years have furnished us with volumetric methods which

leave nothing more to be wished for. This leads us to hope that in scientific, as well as in technical chemistry, the volumetric method will continue to gain ground; nay, it is even expected by many, that in many respects the usual mode of analysis may be completely superseded by the volumetric.

Volumetric analysis has made considerable progress in consequence of the endeavours that have been made to combine the various methods of determination, often differing so much from each other, in as few as possible, so as to enable a considerable series of bodies to be ascertained. A further progress consists in the endeavour to find reagents, which not only furnish a sufficiently exact result, but which may also be readily obtained in a state of purity, and which are not liable to change when kept long in solution. But amongst the reagents which agree with this description, there are but few which are at the same time adapted for general employment; so that the problem to be solved in this case was, the finding of such reagents as would unite exactitude, purity, and stability in solution with general applicability. I believe that we shall find a reagent, combining all these requisites, in the bichromate of potash, first employed by Penny*; and I will therefore, in the present memoir, bring together the results which I have obtained by means of this compound, in the determination of a considerable series of important bodies. At the same time, the exactness of the analyses may serve as a contradiction to the objections urged by Schwartz† against the employment of bichromate of potash. This author objects to bichromate of potash,—1st, because the commercial salt is contaminated by sulphate of potash; 2nd, because permanganate of potash is a far better reagent; and 3rd, because in the determinations put forward by Penny the completion of the reaction is difficult to ascertain.

As regards the last point, the objection is well grounded. The impurities of the bichromate of potash, on the contrary, may be got rid of in the simplest manner by repeated crystallization, an operation which can present no difficulties to any manufacturer. The preparation of permanganate of potash may well however present many difficulties to any one; for, in the first place, the oxide of manganese employed in its production is never pure; in the second, the temperature, during the calcination with chlorate of potash and caustic potash, must always be kept within certain bounds, as when it rises too high the manganate of potash already formed may be destroyed, whilst at too low a temperature the chlorate of potash is not completely decomposed, and the latter is particularly difficult to separate from the permanganate by crystallization; 3rd, the solution of permanganate of potash must be freed from the peroxide of manganese formed, but at the same time the employment of a filter or of any organic substance for this purpose must be carefully avoided; and 4th, if the permanganate of potash is to be obtained pure, it

* Quart. Journ. Chem. Soc., iv. 239.

† Pract. Anleit. zu Maassanalysen, von Dr. H. Schwartz. 2nd edition, pp. 119 and 133.

must also be recrystallized, an operation which is attended with much more difficulty with a body so readily decomposable than with chromate of potash.

Another difficulty attending the employment of the permanganate, which can only be provided against by the most careful preservation, is caused by its ready decomposability; if it be necessary to operate frequently with this substance, particles of organic dust may penetrate into the bottle every time it is opened, and even the smallest portion of these is sufficient to produce partial decomposition of the solution. And if the quantity of permanganate of potash in the solution is to be ascertained before each experiment, iron wire must be weighed and dissolved in muriatic acid, which always causes a loss of time.

On the other hand, bichromate of potash may always be obtained perfectly pure; it may even be completely freed from its hygroscopic water by fusion without any fear of decomposition, so that it may furnish a solution of which the exact strength may be known, and which may be kept for a long time without the least decomposition, even in contact with organic substances. Lastly, results may be obtained in a very simple and certain way with this substance, which are in no way inferior to those obtained by means of permanganate of potash.

There is yet another thing to be thought of in these analyses. In all volumetric methods it is one of the principal problems, to determine exactly the point at which the reaction is completed. In analyses by precipitation this point is attained when nothing more is thrown down; in analyses by oxidation and reduction it is generally known by changes of colour. The latter however do not always furnish any point at which the reaction can with certainty be regarded as complete; but there are generally transitions from one colour to another, so that doubt may prevail as to the completion of the experiment. It is only very recently that methods have been introduced, by which it is possible to determine almost exactly the point at which the reaction is concluded. The property of iodine, even in the smallest quantities, of giving with starch-paste a blue colour of so intense a quality that other colours are concealed by it, has been made use of by Bunsen in his memoir "Upon a Volumetric Method of very general applicability*," to show the completion of the reaction, and indicate the results of his experiments as exactly as this point can be determined.

I have also availed myself of this property of iodine; as bichromate of potash expels iodine from hydriodic acid, and the former then gives a blue colour with starch-paste, in case no reducing substance is present, which must be oxidized by the bichromate of potash before iodine can be separated from the hydriodic acid. Such a reducing substance, amongst others, is protochloride of tin, so that, if a piece of iodide of potassium, or a few drops of a solution of that salt, be added to a strongly acid solution of chloride of tin, together with diluted starch-paste, and a solution of bichromate of

* Ann. der Chem. und Pharm., lxxxvi. p. 265.

potash be then dropped into the mixture, each drop as it falls will produce a separation of iodine, which however immediately disappears in consequence of the action of the chloride of tin; the fluid gradually acquires a slight greenish colour from the formation of chloride of chromium, until a point is arrived at when the addition of only a single drop of the solution of bichromate of potash instantaneously causes the whole to assume an intense blue colour, and to lose almost all its transparency. At this point the reaction is completed, that is to say, all the protochloride of tin is converted into perchloride. All the determinations given in the following pages are founded upon the strongly reducing action of the protochloride of tin, and the readiness with which the quantity of this salt contained in a solution may be ascertained quickly and with certainty by the employment of bichromate of potash.

For this purpose the following fluids are necessary:—

1. A solution of bichromate of potash. To prepare this, the commercial salt must be purified by repeated crystallization, heated in a porcelain crucible until it is fused, and cooled over chloride of potassium. The solid mass falls to pieces so completely, that a fine powder is obtained, which consists entirely of small aggregations of crystals. Ten grammes of this powder are to be weighed, and dissolved in from $\frac{1}{2}$ to 1 litre of water, so that 1 cub. centim. of the solution may contain 0·02 or 0·01 grm. of the solid chromate.

2. A solution of protochloride of tin, prepared by dissolving good commercial tinfoil in concentrated muriatic acid, and diluting this solution with two or three times the quantity of water. The strength of this solution of chloride of tin must be ascertained by means of the bichromate of potash, before every experiment.

3. A solution of iodide of potassium of any desired strength.

4. A clear solution of starch, which may easily be prepared before every experiment by boiling a little starch with water.

Determination of Tin.

As I have already stated, bichromate of potash has been employed by Penny for the determination of protochloride of tin. He added the solution of bichromate of potash to that of the chloride of tin until a drop taken out either furnished a precipitate with acetate of lead, or produced a red colour with sulphocyanide of potassium and pure sulphate of iron. This operation takes up a great deal of time, and must be performed with great care, to find the point at which the reaction is completed. I have consequently preferred ascertaining this point by iodide of potassium and starch. The following is the process:—

A certain quantity of the substance to be examined for metallic tin or protochloride of tin is to be weighed and dissolved by boiling in muriatic acid. The solution is then poured into a beaker-glass; a few drops of solutions of iodide of potassium and starch are added to it, and the solution of bichromate of potash is then dropped into the mixture from a burette, the whole being constantly stirred. This is continued until the mixture suddenly acquires a blue colour,

from the formation of iodide of starch, becoming at the same time almost opake, when the green colour of the solution of chloride of chromium is completely covered by the blue; this point is recognized with more certainty when the beaker is put upon white paper.

The reaction takes place according to the following formula:—

$$3SnO + Cr^2O^6 = 3SnO^2 + Cr^2O^3.$$

The quantity of tin is then calculated from the quantity of solution of bichromate employed, in the following manner:—

C=the number of cubic centimetres of the solution of bichromate of potash consumed.

c=the quantity of solid bichromate in 1 cub. centim. of solution.

A=the quantity of the substance containing tin employed in the experiment.

x=the per-centage quantity of tin; thus

$$x = \frac{3Sn \,.\, 100 \,.\, c \,.\, C}{KO, Cr^2O^3 \,.\, A}.$$

If exactly $\frac{100c}{A}$ grm. of the substance is weighed off, the formula

$$x = \frac{3Sn \,.\, cC}{KO, Cr^2O^3}$$

gives directly the per-centage quantity of tin.

If it be desired to ascertain the amount of pure protochloride of tin in the commercial article, the formula

$$x = \frac{100 \,.\, 3SnCl \,.\, cC}{KO, Cr^2O^3 \,.\, A}$$

gives the per-centage amount of SnCl.

When chloride of tin is to be examined for the entire quantity of tin contained in it, a weighed quantity must be dissolved in muriatic acid, the tin precipitated by zinc, and this again dissolved in muriatic acid. The protochloride of tin thus obtained is determined as already described.

As Penny came to the conclusion, from an extensive series of experiments, that the atomic weights both of tin and chromium are not exactly determined, he ascertained by direct experiments the quantity of bichromate of potash, which exactly represents 100 parts of tin. From the average of his experiments, it appeared that 83·2 parts of KO, Cr^2O^3 correspond with 100 parts of tin.

As I also arrived at the same result from numerous experiments, I consider that we may substitute these numbers for the equivalents of tin and bichromate of potash in the above formula; this would then take the following form:—

$$x = \frac{100 \,.\, 100 \,.\, c \,.\, C}{83{\cdot}2 \,.\, A}.$$

1 grm. of commercial tinfoil, tested in the way described, gave—

$$A = 1, \quad C = 40{\cdot}25, \quad c = 0{\cdot}02.$$

Amount of pure Tin.

Volumetric analysis.	Ordinary analysis.
96·75	96·85.

In order to produce a more rapid solution of the tin, which dissolves but slowly in muriatic acid, the fluid was first heated almost to boiling, and a drop of very dilute solution of chloride of platinum was then added to it; a trace of metallic platinum was deposited upon the tin, when the solution was so hastened, with strong evolution of gas, that within a few minutes the whole of the tin was dissolved. The small quantity of perchloride of tin which had been formed in consequence of the addition of the chloride of platinum, was soon redissolved by the excess of tin.

Determination of Chromic Acid.

For this purpose a certain quantity of the chromate under examination is weighed, and put into a flask. A large burette is filled with solution of chloride of tin, an excess of which is then poured to the chromate, and after the addition of some muriatic acid the whole is heated for some time. In this manner the chromic acid is reduced to oxide, and a portion of the chloride of tin is converted into perchloride. It is now poured into a beaker; iodide of potassium and starch are added to it, and the quantity of chloride of tin added in excess determined by the standard solution of bichromate of potash. The quantities of the solutions of chloride of tin and bichromate of potash employed are then ascertained, and the strength of the tin solution in chloride of tin determined by pouring 10–20 cub. centims. of it into a beaker, and testing it with the solution of bichromate. The following formula serves for the calculation of the chromic acid in the substance under investigation:—

G=the number of cubic centimetres of solution of tin required for the reduction of the chromic acid.

g=the number of cubic centimetres of the same solution employed in testing its strength in tin.

K=the number of cubic centimetres of chromic solution necessary for the oxidation of the excess of the tin solution.

C=the number of cubic centimetres of chromic solution required for the oxidation of g.

c=strength of the chromic solution.

A=quantity of substance employed.

$$x = \frac{2CrO^3 \cdot 100 \cdot 100 \cdot cC}{3Sn \cdot 83{\cdot}2 \cdot A} \left(\frac{G \cdot C}{g} - K \right).$$

A=1 grm. PbO, CrO^3, G=52·25, K=28·55, g=9·05, C=12·85, c=0·01.

	Found.	Calculated.
PbO	67·99	68·29
CrO^3	31·01	31·71

Determination of Copper.

Copper may be determined in the same manner as tin; protochloride of copper also destroying the iodide of starch produced by the solution of bichromate of potash from iodide of potassium and starch, as long as any protochloride is present. The following is the process:—

The substance containing copper is dissolved in water; or, if it be insoluble in this fluid, in an acid. If it be necessary to employ nitric acid (as, for instance, with copper pyrites), this must be as far as possible destroyed by evaporation with muriatic acid. Carbonate of soda is then added first of all until a weak acid reaction is produced, then sugar of milk or grape-sugar, and the whole is gently heated; lastly, an excess of potash is added, and the fluid digested at a *moderate* heat until all the copper is precipitated in the form of protoxide, that is to say, until the precipitate has become reddish-brown and the supernatant fluid colourless. An excess of muriatic acid is then added, and the whole is allowed to cool, when it is put into a beaker, mixed with iodide of potassium and solution of starch, and the solution of bichromate of potash added to it until the blue colour is produced. The reaction may be represented by the following formula:—

$$3Cu^2O + Cr^2O^6 = 6CuO + Cr^2O^3.$$

From this analysis the calculation may be readily effected by the following equation, in which the symbols have the same signification as in the determination of tin:—

$$x = \frac{100 \cdot c \cdot C \cdot 6Cu}{KO, Cr^2O^3 \cdot A}.$$

In this analysis it was to be feared that the presence of an organic substance might also have a reducing action upon the bichromate of potash; but the contrary is proved, not only by the results of several analyses, but also by direct experiments.

Thus sugar was dissolved in water, and boiled with potash, and a drop of solution of bichromate of potash afterwards added to the fluid whilst still hot. It acquired a yellow colour, and on the addition of muriatic acid the original colour of the salt was restored. If a reduction had taken place, it would have been indicated by the green colour of the chloride of chromium. Neither had the protiodide of copper, formed on the addition of the iodide of potassium, any injurious effect; for in the presence of a sufficient quantity of muriatic acid, the protiodide of copper is dissolved, and is also more highly oxidized by the chromic solution.

In order to check the method, sulphate of copper was purified by repeated crystallization, dried for twenty-four hours at 212° F. so as to deprive it of all water, and then treated as above described.

A = 1 grm. CuO, SO^3.
C = 15·65.
c = 0·02.

	Found.	Calculated.
Per-centage of copper	39·98	39·75

[To be continued.]

Note on a Process for the Determination of Copper in Minerals and Artificial Products. *By* M. L. Rivot.

The author having found that all the principal processes for the determination of copper in minerals and alloys were liable occasionally to lead to error, has adopted a new method, which is founded on the insolubility of the sulphocyanide of copper, CyS^2Cu^2, and the great solubility of the sulphocyanides of all the other metals, in acid fluids. It consists in the three following operations:—

1. All the metals contained in the substance under examination are dissolved in muriatic acid, avoiding the use of oxidizing agents.

2. The salt of copper is brought to a minimum by means of a reducing agent (hypophosphorous or sulphurous acid), and a dilute solution of sulphocyanide of potassium is poured to it; this immediately precipitates the copper alone.

3. The metal is determined by drying the sulphocyanide thus obtained at a moderate heat. The determination may be checked by converting the sulphocyanide into sulphuret of copper, Cu^2S, by fusion with a little sulphur in a porcelain crucible, from which the air must be excluded.

This process may be simplified when the substance to be examined contains no metals (besides copper) precipitable by sulphuretted hydrogen. In this case the solution of all the metals is effected by muriatic acid, and the copper precipitated by sulphuretted hydrogen. The precipitate is converted into sulphuret of copper, Cu^2S, by fusion with a little sulphur.—*Comptes Rendus*, May 15, 1854, p. 868.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the various Means of preventing the Formation of Incrustations in Steam-boilers.

The following is for the most part an abstract of a recently-published work by Dr. Elsner, "On the means hitherto employed in preventing the production of Crock in steam-boilers, with the addition of some original observations upon this subject;" and we have added some information obtained from other sources. Those who wish for more complete information, we must refer to the little memoir of Dr. Elsner's, just quoted.

The different means for the prevention of the formation of crock are arranged chronologically, *i. e.* in the order in which they were made known:—

1. *Potatoes.*—Of these, one-fiftieth of the weight of the water is said to be sufficient to prevent the incrustation. According to Elsner, crusts already formed are not removed by potatoes. The action is mechanical; the calcareous particles, when separated, becoming coated with the slimy matter of the potatoes, which prevents their forming a coherent deposit.

2. *Fatty Oils, Tallow.*—Oil, when poured into the water, is said to prevent incrustation. According to Kennedy, the inside of the boiler should be well rubbed with a mixture of 3 parts of black lead and 18 parts of tallow. Newton recommends 1 part of tallow, 1 part of black lead, and $\frac{1}{8}$th part of powdered charcoal. The statements as to the degree of protection afforded by this agent are satisfactory.

3. *Sawdust.*—Roard recommended mahogany sawdust. 20 litres of this were put into a boiler, and no deposit was formed in three months. Ira Hill replaced the mahogany dust by oak dust, and any other wood will serve equally well. The disadvantage of this preventation is the readiness with which the sawdust may be carried into the pipes, cocks, valves, &c., where it might produce evil consequences. The action of the sawdust is also mechanical.

4. *Clay*, free from sand, and worked up with water, is recommended by Chaix. Aldefeld found that this agent prevented the formation of crock; but that, on the other hand, it produced a slimy coating in the pipes, and rendered the steam-cylinder rough. Its action is also mechanical.

5. *Ammoniacal Compounds.*—Ritterbrand, in 1844, patented certain ammoniacal compounds, especially muriate of ammonia. Elsner regards this proposition as the most deserving of notice. As much muriate of ammonia is added to the water as it contains carbonate of lime in solution. This agent also softens old incrustations, but for this purpose something more than the quantity just mentioned is required. Its action is chemical; from the muriate of ammonia and sulphate or carbonate of lime, are formed chloride of calcium and sulphate or carbonate of ammonia. The latter salt is somewhat volatile; if the steam is to be employed in heating colour baths, it is necessary to ascertain carefully whether the volatile alkali will have an injurious action. Elsner states that 1 lb. of muriate of ammonia is sufficient for 20 cubic feet of a well-water containing gypsum. Muriate of ammonia is preferable to carbonate of ammonia. In the 'Verhandlungen des Holländischen Ingenieurvereins,' there are two papers on the employment of muriate of ammonia. The first, by A. A. C. de Vries-Robbé, shows, that in the locomotives on the Dutch railways 2 oz. of muriate of ammonia for each boiler is sufficient to clean incrusted boilers in a few days. This quantity, put in twice a week, keeps the boiler quite clean; iron and copper are not dissolved by it. The second paper, by C. Scheffer, states that in the royal wood-cutting establishment of Holland a perfectly clean boiler was supplied weekly for four months with $\frac{2}{10}$ths of a pound of muriate of ammonia, when 40 lbs. of crock were found to have deposited. The boiler was worked fourteen hours daily with water containing gypsum.

With the addition of $\frac{4}{10}$ths of a pound of muriate of ammonia twice a week for five months, with the same amount of daily work and the same water, 60 lbs. of crock had deposited. In both cases the deposit was more upon the sides than upon the bottom of the boiler, and much less than without the use of the sal-ammoniac.

6. *Mixture of Extract of Tannin.*—J. Delfosse patented a mixture

of 12 parts chloride of sodium, $2\frac{1}{2}$ parts caustic soda, $\frac{1}{8}$th extract of oak-bark, $\frac{1}{2}$ of potashes, for the boilers of stationary and locomotive engines. The principal agent in this appears to be the tannin of the extract of oak-bark. Elsner recommends the roughly-cut root of the common tormentil for this purpose, on account of the large quantity of tannic acid it contains.

A patented process is now in use in England, which must be mentioned here. *Spent tanner's bark* is put into the boiler. To avoid the chance of the bad result already referred to with the sawdust, the bark is put into a perforated vessel, which is suspended near the surface of the water, and kept in the right position by means of a float. The bark is renewed from time to time. The patentee supplies the whole apparatus for about £2 10*s.*, and publishes many testimonials to show that his process is perfectly successful.

7. According to Cave, *pieces of oak-wood*, suspended in the boiler and renewed monthly, prevent all deposit even from waters containing a large quantity of lime. The action must depend principally upon the tannic acid.

8. *Starch-sugar Molasses, Syrup.*—Guinon put into a boiler, $17\frac{1}{2}$ feet long and $3\frac{1}{2}$ feet in diameter, 5 kilogrms. of molasses every two months; he found that this completely prevented incrustation.

Guimet proved the advantage of this process, but employed brown starch-syrup, 3 lbs. every six months for a boiler of eight-horse power.

9. *Tin Salt* (chloride of tin) is recommended by Delandre; it is similar in its action to muriate of ammonia; but as it is cheaper, it is to be preferred.

10. *Soda* and *Potash* have been recommended by Kuhlmann, and more recently by Fresenius. According to the latter, the property of forming crust occurs more with water containing gypsum than with that containing chalk.

Kuhlmann recommended the addition of 100 to 130 grms. of soda monthly to every horse-power with water containing sulphate of lime. Elsner observes that too much soda might injure the solderings and joints. Zimmer, of Frankfort, who long employed this method, found that the boiler was strongly acted upon; he ascribes this to the presence in almost all sodas of cyanide of sodium, which possesses the power of dissolving iron.—*Schweiz. Gewerbebl.*, 1854, p. 37.

On Vegetable Bronze-colours from Brazil-wood and Logwood. *By* L. Denzer.

When alum is dissolved by heat in a decoction of Brazil-wood, which has been cleared by standing for several days, a precipitate is produced on the cooling of the solution, which increases in proportion to the length of time the fluid is left standing, and at last contains nearly all the colouring matter. If this precipitate be washed once with water, and spread in a tolerably thick coating upon paper, it dries with a beautiful shining gold colour, with a slight tendency

to green, very like the dried wing-cases of the common *cantharides*. If the precipitate be made into a paste, mixed with a little size and glaze (prepared by dissolving wax in soap), and then laid on the paper by means of a brush, it may be polished with an agate or glass ball, and then acquires a beautiful yellow metallic lustre, exactly like bronze. It is however necessary for this purpose, that the paper should be so thickly coated with the colour as to render it quite opake.

A colouring matter obtained from logwood has exactly the same properties, but its preparation is somewhat different, and the metallic lustre has more of a coppery tint, the former rather resembling brass.

If a freshly prepared concentrated decoction of logwood be heated in a copper kettle, and then mixed with chloride of tin, an abundant dark brown precipitate is obtained, which is to be collected without washing. This precipitate, when employed like the preceding one, communicates a copper-bronze colour to paper. A different shade is obtained when the hot decoction of logwood is first mixed with a little alum, and afterwards with a still smaller quantity of bichromate of potash; this precipitate is darker, and its lustre, when laid on paper, has more of a yellowish tinge, so that it forms an intermediate shade between the other two colours.

All these precipitates are particularly adapted for the fabrication of marbled papers and paper-hangings; for if the mixture of the size, glaze, and colour is well effected, the metallic lustre makes its appearance even on rubbing with a stiff brush.

As a guide in the preparation of these colours, I give the following formulæ:—

1. 10 lbs. of good Brazil-wood are deprived of their colouring matter by repeated decoction in river-water, and the collected decoctions left standing for from four to eight days in an open wooden tub. The clear decoction is then poured away from the sediment, and put again into a clean vessel. Part of it is then heated, and whilst hot 5 lbs. of alum are dissolved in it, and the solution is mixed with the remainder. The precipitate will have collected in about eight days; it is strained through cloth till it acquires a pasty consistence, and preserved for use in that form.

2. 10 lbs. of logwood are boiled twice with river-water, and the strained decoction evaporated to one-half in the kettle; 10 oz. of chloride of tin are then added, and the precipitate is strained through cloth.

3. The decoction is prepared and concentrated as before, and 10 oz. of alum are added to it, and allowed to dissolve; powdered bichromate of potash is then sprinkled in gradually as long as a sample taken out and laid on paper still appears dark blue; for this purpose $1\frac{1}{4}$ oz. are generally required. Too much of the bichromate of potash renders the colour black, and spoils it. This is also strained through cloth.—Dingler's *Polyt. Journ.*, cxxvi. p. 433.

THE CHEMICAL GAZETTE.

No. CCLXXXII.—July 15, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Bismæthyle and its Compounds. *By* F. Dünhaupt.

Bismæthyle was discovered by Löwig in 1851, and afterwards further investigated by Breed under Löwig's directions*. At the instigation of the same chemist, Dünhaupt has continued the examination of this body, which he has treated of in an inaugural dissertation.

The first step in the preparation of bismæthyle is to prepare an alloy of bismuth and potassium, by heating 5 parts of pure bismuth and 4 parts of tartrate of potash in a covered crucible; this is finely powdered, and treated with iodide of æthyle, the air being excluded; after the completion of the reaction, the mass is put into a cylinder from which the air is expelled by carbonic acid, and extracted with æther, which dissolves the bismæthyle; the æther is then distilled off from a retort containing a little boiled water, and it is advisable during this process to pass carbonic acid gas through the distilling apparatus, in order to prevent the formation of hydrated oxide of bismuth. When the distillation is completed, the bismæthyle is left under the water in the retort, and any oxide formed may be easily got rid of by shaking with a little dilute nitric acid. 3 lbs. of alloy and 1 lb. of iodide of æthyle furnish 4 or 5 oz. of pure bismæthyle. In operating upon small quantities, if the air be not sufficiently excluded, or the alloy be wrongly treated, it may readily happen that, instead of bismæthyle, nothing but hydrated oxide of bismuth is obtained.

Bismæthyle, heated by itself in the anhydrous state, is decomposed even between 90° and 108° F.; metallic bismuth is separated, and a permanent gas, probably æthyle gas, is evolved; at 302° F. it is decomposed with a violent explosion. It may be distilled with water or æther. If the dilute ætherial solution be allowed to evaporate very slowly in the air, the residue consists of a white hydrated oxide of bismuth, quite free from organic substance, and containing 88·88 and 88·50 per cent. of oxide of bismuth. The formula BiO^3, 3HO requires 90·00 per cent.

Even when it is attempted to decompose metallic salts by bismæthyle and throw down the metallic oxide, the bismæthyle itself is decomposed. This is the case with nitrate of silver.

* Chem. Gaz., vol. x. p. 201.

Bismæthyle and Sulphur.—When the alcoholic solution of bismæthyle is boiled with flowers of sulphur, sulphuret of bismuth separates; if the fluid be filtered whilst boiling, it deposits a small quantity of a yellowish-brown powder, which still appears to contain organic matter.

When an ætherial solution of bismæthyle is saturated with sulphuretted hydrogen, and left standing in a loosely stoppered bottle, it deposits crystals of BiS^3 of a metallic lustre.

Bismæthyle, which has been long exposed to the air under water, gives first a yellow, and afterwards a brown precipitate with sulphuretted hydrogen. The yellow precipitate also becomes brown when dried, and has the same composition as the brown; when analysed after drying, they are found to have the same composition, corresponding to the formula $BiAe^3S^2+2BiS^3$. Thus the analyses of various similar precipitates gave:—

Bismuth	74·40	73·70	74·62	3 =	624	74·37
Carbon	7·87	8·00	8·00	12	72	8·58
Hydrogen ..	1·93	1·84	1·84	15	15	1·78
Sulphur	15·20	15·10	15·00	8	128	15·27

Bismæthyle and Iodine.—When iodine is added to the alcoholic solution of bismæthyle until the colour of the iodine no longer disappears, the substances which separate are sometimes red, sometimes yellow, according to the strength of the solution. Various compounds are contained in the solution. If an alcoholic solution of iodine be added to an alcoholic-ætherial solution of bismæthyle until the colour of the solution of iodine begins to be permanent, and a small quantity of water be then added, an amorphous precipitate, sometimes of a yellowish, sometimes of a reddish colour, is immediately thrown down. If it be filtered now, and a tolerably large quantity of alcohol be added to the filtrate, an amorphous reddish-yellow precipitate is again produced. If this be quickly filtered, and the filtrate mixed by constant stirring with a considerable quantity of water, a red precipitate of acicular crystals is immediately produced, which must be dried in the absence of light, as it would otherwise be decomposed. The analysis of this compound led to no decided result.

An *iodide*, $Bi^3Ae^3I^5$ or $(Bi^2Ae^3)I^2+BiI^3$, is obtained when iodine is added to a tolerably concentrated alcoholic solution of bismæthyle until the colour of the former disappears, the fluid filtered from the precipitate, and a large quantity of water at 104° F. added to the filtrate. A small quantity of a ruby-coloured fluid is then separated; and if the watery fluid be poured away from this, a large quantity of beautiful red acicular crystals are formed during its cooling; these must be immediately collected, and dried *in vacuo*. This compound is but sparingly soluble in water, but dissolves pretty readily in alcohol and æther; its solutions have a pale yellow colour. When heated on platinum foil, a strong yellow vapour is first evolved, which takes fire on contact with flame. The same compound is obtained when bismæthyle is left for a considerable

time in contact with dilute nitric acid, and then mixed with iodide of potassium. Its analysis gave,—

Bismuth....	46·47	46·00	46·49	46·42	3	624	46·37
Carbon	4·58	4·91	..	..	12	72	5·35
Hydrogen ..	1·43	1·57	..	..	15	15	1·11
Iodine	47·17	47·00	46·96	47·12	5	635	47·17

There is also probably an iodine compound, $BiAe^4I+2AeI$, which is very unstable; it is contained in the ruby-coloured fluid above mentioned.

Bromine and Bismæthyle.—A compound, $BiBr+2BiAe^3$, is formed when an alcoholic solution of bromine is added to an alcoholic solution of bismæthyle until the colour of the former is no longer lost, and the whole is then mixed with water. A white powder, of the above constitution, is thrown down, and the fluid becomes acid. From this acid solution sulphuretted hydrogen throws down yellow precipitates, which soon become brown, and which have the composition $BiAe^3S^2+2BiS^3$. The white powder, when dried, contained 68·88 bismuth, and 26·88 bromine.

Bismæthyle and Perchloride of Mercury.—If an alcoholic solution of bismæthyle be added to a not too dilute alcoholic solution of perchloride of mercury, the former being poured slowly and constantly stirred into the mercurial solution, a very large precipitate of protochloride of mercury is immediately obtained, and no doubt chloride of bismuth and chloride of æthyle are formed simultaneously. But if the process be reversed, and a hot dilute alcoholic solution of perchloride of mercury be poured in a thin stream and with constant stirring into a dilute alcoholic solution of bismæthyle, to which a few drops of muriatic acid have been added to prevent the separation of oxide of bismuth, no precipitate is produced at first; but after some time a voluminous light precipitate is formed, which however is again completely dissolved if the fluid be heated. The reaction is terminated when a drop of the fluid no longer produces a white precipitate in a solution of perchloride of mercury; as long as this is produced, undecomposed bismæthyle is present. By a little care, it may be very exactly arranged that neither perchloride of mercury nor bismæthyle should predominate. The whole is then heated upon the water-bath until a perfectly clear solution is obtained; and in case (as sometimes happens) a small quantity of metallic mercury has separated, the fluid is to be poured away from it. On the cooling of this fluid, light crystalline laminæ of a silvery lustre are deposited, which exhibit a beautiful iridescence by reflected light, and gradually fill the whole fluid. These crystals, as the author ascertained by analysis, consist of chloride of hydrargyræthyle $=(Hg^2Ae)Cl$; the solution from which they have been formed contains the chloride of a new radical, $(BiAe)Cl^2$. No other products, at least primary, are formed. When the chloride of hydrargyræthyle has been separated by filtration, if bismæthyle be again added to the filtrate, and this be afterwards treated in the same manner as before with solution of perchloride of mercury, this

operation may be repeated three or four times in an hour; and by this means 15 to 20 grms. of chloride of hydrargyræthyle may be prepared in that time. The decomposition takes place according to the following equation:—

$$4HgCl + BiAe^3 = 2(Hg^2\,Ae)\,Cl + BiAeCl^2.$$

The author proposes the name of *bisæthyle* for the radical BiAe: and for that mentioned in the preceding as bismæthyle, $BiAe^3$, the name of *bistriæthyle.*

Iodide of Bisæthyle, $(BiAe)\,I^2$.—The solution from which the chloride of hydrargyræthyle was deposited acquires a yellowish-red colour on the addition of iodide of potassium, without becoming turbid. If it be mixed with water until turbidity is produced, and then heated on the water-bath, a perfectly clear solution is obtained, which is allowed to cool gradually. During cooling, beautiful six-sided laminar crystals of a golden-yellow colour separate. These are pressed between blotting-paper, and dried *in vacuo*; in this condition they possess a perfect golden lustre. This body is the chloride corresponding with the iodide $(BiAe)\,I^2$; it is scarcely soluble in water, and is difficult of solution even in æther, to which it gives a pale yellow colour; it dissolves pretty readily in alcohol, even when hydrated, with the assistance of a moderate heat. Analyses:—

Bismuth ..	42·20	41·96	42·31	42·57	42·49	1	208	42·36
Carbon ..	5·21	..	..	..	..	4	24	4·88
Hydrogen	1·35	..	..	..	..	5	5	1·03
Iodine	50·20	50·69	50·47	51·60	..	2	254	51·73

Oxide of Bisæthyle$=(BiAe)\,O^2$.—If solution of potash be added to a solution of the above-mentioned iodide in watery alcohol, a yellowish-white precipitate is produced, which however is redissolved by the slightest excess of potash; ammonia, on the contrary, completely precipitates the oxide, and does not dissolve it again when in excess. If the precipitate be collected immediately upon a filter, washed several times with absolute alcohol, then pressed and dried *in vacuo* over sulphuric acid, it appears, when examined under the air-pump, to be an amorphous yellow powder; but immediately it is brought from the vacuum into the air, it ignites with formation of a dense yellow vapour. Its analysis is of course impossible; its theoretical composition is,—

Bismuth	1	208	82·21
Æthyle.....	1	29	11·46
Oxygen	2	19	6·33

It appears also that when bistriæthyle is converted into $BiO^3, 3HO$ by spontaneous oxidation, it first passes, with elimination of 2 atoms of æthyle, into $(BiAe)\,O^2$.

The compounds of bisæthyle are only to be obtained with great difficulty, as this radical, like bistriæthyle, is characterized by its great decomposability; the iodide alone is stable, when preserved in a perfectly dry state, in the dark. If it be left standing in a dark place for a considerable time under the mother-liquor from which it

separated, and which still contains an excess of iodide of potassium, the red crystals disappear, and become converted into small, black, metallic, crystalline granules of iodide of bismuth, BiI^3, whilst the supernatant fluid still retains a strong yellow colour.

Chloride of Bisæthyle, $(BiAe)Cl^2$, is contained in the alcoholic solution obtained by the action of bistriæthyle upon perchloride of mercury. If the solution be evaporated on the water-bath to a small residue, it remains perfectly transparent; on cooling, a little chloride of hydrargyræthyle separates, which must be got rid of by filtration. If the filtrate be allowed to evaporate spontaneously, small white crystals are obtained, which no doubt are the chloride of bisæthyle. They do not however dissolve completely in water, but leave behind them a white powder; the addition of solution of iodide of potassium to the dissolved portion produces $BiAeI^2$, which crystallizes from the warm solution in fine golden-yellow laminæ, a sufficient proof that unchanged chloride of bisæthyle was still present in the solution. This compound consequently consists of,—

Bismuth	1	208	67·55
Æther	1	29	9·42
Chlorine	2	71	23·05

By treating iodide of bisæthyle with nitrate of silver, sulphate of silver and sulphuretted hydrogen, the author obtained the salts $BiAeO^2, 2NO^5$; $(BiAe)O^2, 2SO^3$; $(BiAe)S^2$.—*Inaugural Dissertation*, Breslau, 1854.

On the Decomposition of Phosphate and Sulphate of Lime by Muriatic Acid. By M. Cari-Mantrand.

A mixture of equal parts of bone-ashes and wood-charcoal powder, heated to redness in a porcelain tube, through which gaseous muriatic acid is passing, immediately furnishes phosphorus, which condenses in the cooled portion of the tube, while oxide of carbon goes off. This decomposition probably takes place in accordance with the following equation:—$PO^5, 3CaO + 8C + 3HCl = 8CO + 3CaCl + 3H + P$. No trace of phosphoric acid was found in the residue. The hydrogen of the muriatic acid is passive in this operation, for the same result is obtained by the employment of dry chlorine; this, when its evolution is well regulated, is completely absorbed, forming chloride of calcium and phosphorus, and the action is still more rapid than with muriatic acid.

Sulphate of lime, mixed with charcoal, and treated in a similar manner with a current of muriatic acid, furnished chloride of calcium, oxide of carbon, sulphur and a little sulphuretted hydrogen.

Even without any addition of charcoal, sulphate of lime allows sulphuric acid to escape when heated in muriatic acid gas; a portion of it is decomposed into sulphurous acid and oxygen, and chloride of calcium is formed.—*Comptes Rendus*, xxxviii. p. 864.

On the Constituents of Pollen. *By* MM. E. Fremy *and* Cloez.

According to the authors, pollen has a remarkable analogy in its composition to oleaginous seeds. In pollen, as in the latter, there are membranes containing more or less nitrogen, starch, a kind of diastase, fatty oil and much albuminous matter. The protrusion of the pollen-tube is compared by the authors with that of the germinative process of seeds.

Waxy Matter.—The pollen of *Lilium croceum* (*Lys orangé*) contains a large quantity of a waxy substance, which was taken up by means of æther. The æther extracts nothing from the interior of the grain, so long as this is uninjured. The waxy matter can only be saponified with difficulty by potash. It has a yellow colour, which very quickly disappears when exposed to the light; this wax may also be a constituent of the ordinary yellow wax. Its analysis gave,—

Carbon	79·53	79·65
Hydrogen	12·00	12·09
Oxygen	8·46	8·26

The following experiments were made with the pollen of white and yellow lilies.

Starch, Dextrine, Sugar.—Boiling water extracts dextrine from pollen, and this is converted by heat into grape-sugar. As iodine produces a blue coloration in pollen after some time, there must, the authors conclude, be a substance in the pollen similar to starch.

Albumen is contained in the watery extract of pollen.

Oil.—Æther extracts fatty oil from the crushed pollen-grains. The analysis of this oil gave,—

Carbon	75·36
Hydrogen	12·90
Oxygen	11·74

The membranes of the pollen, as they remained after its treatment with water, alcohol and æther, furnished on analysis the results shown in column I. In consequence of the large amount of nitrogen, the mass was again treated with potash, to extract all albuminous matter, and then again analysed. The results are given in column II.:—

	I.	II.
Carbon	52·25	56·05
Hydrogen	7·38	7·55
Nitrogen	10·83	6·12
Oxygen	29·54	30·28

The membranes consequently always contain a considerable quantity of nitrogen. The albuminous matter dissolved in the potash gave on analysis,—

Carbon	50·06
Hydrogen	7·28
Nitrogen	12·46
Oxygen	30·20

Journ. de Pharm. et de Chim., 3rd ser. xxv. p. 161.

On the Formation of Indigo in the Human Organism.
By H. von Sicherer.

A careful examination of the urine in which this colouring matter was produced without intermission, exhibited no abnormal conditions with respect to the amount of uric acid, urea, chloride of sodium, phosphates, &c., contained in it. Bile could not be detected in it, and it was of the usual wine-yellow colour. It was frequently turbid, and then deposited, together with mucus, another sediment, which was shown by the microscope to be urate of soda. The use of various kinds of food and beverages produced no observable changes in it.

The existence of the blue colouring matter was never betrayed by spontaneous deposition from the urine, either when fresh or after long standing, although this was observed by Hassall, and always takes place in Bright's disease. The colouring matter was only separated on the addition of almost an equal quantity of fuming muriatic acid, or dilute sulphuric or nitric acid, the urine gradually acquiring a reddish-brown colour, and at last becoming quite opake, when the colouring matter made its appearance either as a deep blue froth immediately after shaking, or as a thin reddish-blue film when it had been left standing some time. The coloration of the urine is rendered particularly distinct by sulphuric acid when it spreads from above; and it is clear that in such a case Pettenkofer's test for bile may easily lead to errors.

After standing for forty-eight hours, acids separated no more blue pigment from the urine, even after preliminary evaporation; and this was the case even when the evaporation was effected with the air excluded by a current of carbonic acid gas.

The colouring matter, when washed and dried, forms a deep blue powder with a coppery tinge. It is insoluble in cold and boiling water, dilute acids and alkalies; but is dissolved by boiling alcohol, and still more readily by æther, to which it communicates a blue colour. On the cooling of the saturated solutions, however, the greater part of it separates in the form of a blackish-blue powder, whilst the supernatant fluid appears rather of a violet or reddish colour. By the evaporation of the alcohol, the fluid at last becomes reddish-brown, and then spreads itself like a shining varnish over the remainder of the powder.

But the property which, above all others, this pigment possesses, in common with indigo, is its power of sublimation. At about 537° F. it is converted into a purple vapour, and sublimes, for the most part undecomposed, into shining transparent prisms and needles of a purple colour, which are insoluble in water, alcohol and æther, and cannot be distinguished from sublimed indigo. A part of it is carbonized during the process, evolving an empyreumatic odour. The crystals obtained exactly agree with pure indigo-blue.

With regard to its constitution nothing can be said, except that it contains nitrogen and is very rich in carbon. It is also characterized by a very low specific gravity.

With concentrated sulphuric acid it behaves like indigo, dissolving therein completely with evolution of heat, and furnishing a dark blue solution. It is destroyed by chlorine. Sulphurous acid by itself does not bleach it. When boiled with moderately strong nitric acid, it is decolorized and forms a yellow solution.

This substance is also deprived of its colour (*i. e.* reduced) by readily oxidizable bodies, such as protoxide of iron, sulphurous acid, sulphuret of ammonium, &c., in the presence of alkalies or alkaline earths; and it may be restored with its original colour from the colourless alkaline solution by contact with atmospheric air. In the reduced state it probably agrees with indigo-white.

If we compare the properties of indigo with those just mentioned belonging to Heller's cyanurine or urocyane, the similarity of sublimed cyanurine to indigo-blue, and of its behaviour when heated, and with alcohol, æther, sulphuric acid and reducing agents, is seen to be exceedingly great; but as the composition of cyanurine is still unknown, we must wait for this before we can conclude these two substances to be identical.—*Ann. der Chem. und Pharm.*, xc. p. 120.

On the Preparation of Calomel in the Humid Way.
By Prof. Wöhler.

It has long been known from Vogel's experiments, that protochloride of mercury is precipitated from the solution of the perchloride by sulphurous acid. This behaviour appears to me to be available in the practical preparation of calomel. It is obtained in this manner as a very delicate powder, of a dazzling white colour, which glitters in the sunlight. The difficult process of sublimation and the tedious preparation would thus be avoided; and its preparation in the laboratory would be a very easy matter. It would be obtained immediately in the finely divided state in which the pulverulent sublimed calomel is procured, without any necessity for an operation of so much danger as the preparation of calomel by sublimation, which moreover can only be performed on a large scale. As the calomel formed by sulphurous acid is crystalline, and therefore in the same condition as the sublimed, there can also be no doubt that it will not differ from this in its medicinal efficacy. The crystals may be distinctly recognized, even with a magnifying power of only 100 diameters; they are generally united, forming regular crosses.

For its preparation it is only necessary to dissolve commercial perchloride of mercury in water heated to about 122° F. until this is saturated, and afterwards to pass sulphurous acid gas into the hot solution. The gas is evolved by heating coarse charcoal powder with concentrated sulphuric acid. The separation of the calomel commences immediately. When the solution is saturated with gas, it is digested for some time, then left to get cold, and filtered from the calomel, which is afterwards washed. The filtrate usually still contains some unchanged perchloride, which may be converted into calomel either by heating to boiling, or by a fresh introduction of sulphurous acid and heating. It still remains to be ascertained what

temperature is the most proper for the conversion of the whole of the perchloride into calomel.—*Ann. der Chem. und Pharm.*, xc. p. 124.

ANALYTICAL CHEMISTRY.

On a Method of Volumetric Analysis of general application.

By D. Aug. Streng.

[Concluded from page 256.]

Determination of Lead.

The volumetric methods hitherto in use for the determination of lead are of such a nature that they can only be employed with very soluble compounds of that metal (white lead, sugar of lead); all insoluble lead compounds were excluded, especially galena and sulphate of lead. As hitherto the only solvent of galena has been nitric acid, by the action of which insoluble sulphate of lead is always produced, no means were known by which the lead of galena could be determined volumetrically. It is quite recently that Rivot, Beudant, and Daguin* have recommended the employment of chlorine in analysis, referring especially to the decomposing action of this body upon galena in the presence of a free alkali, when it produces sulphuric acid and peroxide of lead. Thus, according to these chemists, when a current of chlorine gas is passed into a solution of potash in which galena is suspended, the reaction just referred to is produced, so that the lead may be readily determined in this manner in the form of peroxide. Availing myself of this statement, I endeavoured to produce the same reaction in a more simple manner by treating galena with solution of chloride of lime. In fact, even when heated, peroxide of lead is formed in considerable quantity; but the decomposition is by no means complete, as, notwithstanding repeated treatment with the solution, the coarser particles of the galena obstinately withstand the action. I therefore tried converting the galena into sulphate of lead by nitric acid, neutralizing the fluid with potash, and then acting with the solution of chloride of lime upon the finely divided sulphate of lead. The conversion was complete; after the fluid had been heated for a considerable time to 203°–212° F., all the lead was converted into peroxide. Care must be taken, however, not to let the sulphate of lead collect into lumps, as otherwise the action cannot penetrate into the inner portion of the little grains. Moreover, it is not only sulphate of lead that can be converted in this manner into peroxide, but nearly all other lead compounds have a similar behaviour.

These properties of the salts of lead were made use of in effecting their determination by the volumetric method. The process is as follows:—

If the substance containing lead be soluble in water or acids, it is

* Chem. Gaz., No. 271. p. 56.

dissolved therein, and then mixed with an excess of potash; in operating with galena, it is completely oxidized by nitric acid, and also supersaturated with potash. Sulphate of lead is powdered as finely as possible, and then treated in the same way. A solution of hypochlorite of lime is then added in excess, and the whole is heated almost to boiling for a considerable time, when all the lead is converted into brown peroxide. The precipitate is put upon a filter, and washed with boiling water, an operation which is very quickly performed; the filter is then broken with a glass rod, and the precipitate thrown into the vessel in which its conversion into PbO^2 was effected. Solution of protochloride of tin is then dropped upon the filter until all the portions of the precipitate still adhering to it are dissolved, and the filter is again washed with hot water; an excess of the solution of protochloride of tin is then added to the dilute fluid thus obtained, by which the peroxide of lead is converted into chloride. Some muriatic acid is now poured in, and heat applied until everything is dissolved, when the following change takes place:—

$$SnO + PbO^2 = SnO^2 + PbO.$$

The clear fluid is poured into a beaker, and mixed with iodide of potassium and solution of starch; the excess of chloride of tin determined by the solution of bichromate of potash. If the quantity of chloride of tin contained in the solution be then ascertained, we have all the necessary data for the determination of the quantity of lead. The formula for the calculation of this analysis is as follows:—

$$x = \frac{Pb \,.\, 100 \,.\, 100 \,.\, c}{83{\cdot}2 \,.\, Sn \,.\, A} \left(\frac{G \,.\, C}{g} - K \right)$$

(the symbols having the same signification as for chromium).

To check this method, the following experiments were instituted:—

1. Pure peroxide of lead, obtained by treating freshly precipitated hydrated oxide of lead with solution of chloride of lime, was filtered after boiling with acetic acid, dried at 212° F., and analysed in the manner above described,—

A=1 grm. PbO^2, G=64·5, g=21·1,
K=98·4, C=39, c=0·02.

	Found.	Calculated.
Pb	85·94	86·67
O.....	14·06	13·33

2. Native galena, containing some copper and iron. Two experiments:—

	I.	II.		Found. I.	Found. II.	Calculated.
A =	1 grm. PbS.					
G =	26·05	19·55	Pb	85·37	85·61	86·66
g =	18·30	15·00	S	14·63	14·39	13·34
K =	26·80	23·60				
C =	33·35	34·05				
c =	0·02	0·02				

The amount of lead, ascertained by the docimastic method, gave 80 per cent., which agrees with the volumetric analysis, as the former always gives 5 per cent. too little.

3. Chemically pure sulphate of lead,—

$G=48{\cdot}30$, $g=23{\cdot}15$, $C=30{\cdot}60$, $K=30{\cdot}5$, $c=0{\cdot}01$.

	Found.	Calculated.
Lead	68·89	68·42

Determination of Manganese.

Manganese occurs in nature in several combinations, amongst which the peroxide occupies the most important place. The determination of this body is an easy task by the method here described. The peroxide is powdered; an excess of solution of chloride of tin is added to it from the burette, and the whole heated with muriatic acid. The whole is thus dissolved, forming protochloride of manganese,—

$$SnO+MnO^2=SnO^2+MnO.$$

The calculation may be effected according to the following formula:—

$$x=\frac{MnO^2 . 100 . 100 . c}{83{\cdot}2 . Sn . A}\left(\frac{G . C}{g}-K\right).$$

Hydrated peroxide of manganese, obtained by treating hydrated oxide of manganese with dilute nitric acid, was dried for a considerable time at 122° F., and analysed:—

$A=0{\cdot}5$ grm. MnO^2, HO, $C=22{\cdot}75$, $K=33{\cdot}5$,
$c=0{\cdot}01$, $G=47{\cdot}05$, $g=13{\cdot}5$.

	Found.	Calculated.
MnO^2	82·61	83·02
HO	17·39	16·98

When any other compound of manganese is to be analysed, the process is the same as for the determination of lead. The compound is dissolved, mixed with an excess of potash, and then with solution of chloride of lime, and the whole digested; the resulting peroxide of manganese is collected on a filter, and reduced by chloride of tin in the same manner as peroxide of lead. The following formula serves for the calculation of the manganese:—

$$x=\frac{Mn . 100 . 100 . c}{83{\cdot}2 . Sn . A}\left(\frac{G . C}{g}-K\right).$$

Determination of Cobalt and Nickel.

The mode of determining these two metals also approaches that for lead very closely. In this case also the compound dissolved in acid is treated with potash and hypochlorite of lime, and the oxide formed (Co^2O^3 and Ni^2O^3) collected on a filter and reduced by chloride of tin:—

$$Co^2O^3+SnO=Co^2O^2+SnO^2.$$

The following is the formula for the calculation of cobalt and nickel:—

$$x = \frac{2Co\,(\text{or Ni}) \cdot 100 \cdot 100 \cdot c}{83{\cdot}2 \cdot Sn \cdot A}\left(\frac{G \cdot C}{g} - K\right).$$

A=0·5 grm. $Co^6 O^7$, obtained by long-continued calcination of the oxide,—

G=46·00, g=11·5, C=19·5, K=46·7, c=0·01.

	Found.	Calculated.
Co	76·48	75·96
O	23·58	24·04

When both oxides are to be determined in the same compound, two methods may be adopted. The first depends upon the dissimilar behaviour of the oxides with ammonia, in which oxide of nickel dissolves. The second is derived from the different behaviour of the two protoxides when exposed to a red heat in contact with air, as under these circumstances protoxide of cobalt absorbs oxygen, whilst oxide of nickel does not do so. I propose to submit these points to a closer investigation in a separate memoir.

Bismuth.

I also hoped to have been able to effect the determination of bismuth in the same manner as the metals already referred to, as this metal also furnishes brown bismuthic acid (BiO^5) in an alkaline fluid with hypochlorite of lime; but either this oxidation is imperfect, or else the formula BiO^5 for bismuthic acid is incorrect, as indeed has been supposed by several chemists; for when I repeatedly treated pure bismuth, prepared from basic nitrate of bismuth, in the same manner as lead, I obtained in several experiments only 65 to 69 per cent. of bismuth. I must therefore for the present give up the determination of this metal.

Determination of Mercury.

The determination of this body is very simple. The substance containing mercury (whether in the form of peroxide or protoxide) is dissolved in muriatic acid; an excess of chloride of tin is then added to it from the burette, and the whole is heated until all the mercury is reduced and collected into solid masses, which takes place at a temperature below boiling. The fluid is then poured from the precipitate into a beaker, the precipitate washed several times, and the excess of chloride of tin employed determined by means of the solution of bichromate of potash:—

$$HgO + SnO = Hg + SnO^2.$$
$$Hg^2O + SnO = Hg^2 + SnO^2.$$

The peroxide and protoxide are calculated by the formulæ I., II.:—

$$\text{I.}\quad x = \frac{Hg \cdot 100 \cdot 100 \cdot c}{83{\cdot}2 \cdot Sn \cdot A}\left(\frac{G \cdot C}{g} - K\right).$$

$$\text{II.}\quad x = \frac{2Hg \cdot 100 \cdot 100 \cdot c}{83{\cdot}2 \cdot Sn \cdot A}\left(\frac{G \cdot C}{g} - K\right).$$

A=1 grm. HgO, G=24·15, g=10·3,
K=13·25, C=24·6, c=0·01.

	Found.	Calculated.
Hg	92·07	92·59
O.....	7·93	7·41

It appears from the preceding, that we have here an entire series of bodies determinable by one and the same method. But if it were required to determine these substances when together, the different behaviour of the peroxides presents an excellent means of separating them from one another. Thus acetic acid dissolves oxide of nickel without decomposition, oxide of cobalt with decomposition; both are also dissolved by nitric acid, whilst peroxide of lead and peroxide of manganese resist the action of this acid. This difference in behaviour may easily be made use of for the separation of these bodies.

Determination of Chlorine and its Oxyacids.

The process for the determination of these substances is founded upon the same principle upon which all the preceding determinations are effected, namely, the reducing action of protochloride of tin.

The substance to be investigated is weighed, dissolved in water, mixed with a known quantity of solution of chloride of tin, and heated. The excess of the latter solution is ascertained by means of solution of bichromate of potash:—

$$Cl + SnCl = SnCl^2$$
$$ClO + HO + 2SnO = ClH + 2SnO^2.$$

Formulæ for the calculation, I. of chlorine, II. of hypochlorite of lime:—

$$\text{I.}\quad x = \frac{Cl \cdot 100 \cdot 100 \cdot c}{83{\cdot}2 \cdot Sn \cdot A}\left(\frac{G \cdot C}{g} - K\right).$$

$$\text{II.}\quad x = \frac{CaO,\,ClO \cdot 100 \cdot 100 \cdot c}{83{\cdot}2 \cdot 2Sn \cdot A}\left(\frac{G \cdot C}{g} - K\right).$$

The formulæ for the other acids of chlorine follow the same rules.

A=0·5 grm. $KO \cdot ClO^5$, G=71·5, g=16,
C=15·85, K=12·25, c=0·02.

	Found.	Calculated.
KCl.....	61·16	60·85
O.....	38·84	39·15

Determination of Iodine.

A known quantity of protochloride of tin is also more highly oxidized by means of free iodine, and the excess of the former determined as above:—

$$I + HO + SnO = IH + SnO^2.$$

$$x = \frac{I \cdot 100 \cdot 100 \cdot c}{83{\cdot}2 \cdot Sn \cdot A}\left(\frac{G \cdot C}{g} - K\right).$$

This process may however be shortened by adding starch-paste to the solution of iodine, and adding solution of chloride of tin carefully until the blue colour disappears on the addition of a single drop. The following analysis is effected in this manner, and calculated according to the formula—

$$x = \frac{I \cdot 100 \cdot 100 \cdot c \cdot C \cdot G}{83{\cdot}2 \cdot Sn \cdot g}.$$

A=0·2387 grm. of iodine dissolved in iodide of potassium,
G=4·45, g=30·45, C=62·05, c=0·01.

	Found.	Calculated.
Iodine.....	0·2388	0·2387

Determination of Sulphurous Acid and Sulphuretted Hydrogen.

The determination of these bodies resembles that of tin, as both have a similar reducing action upon solution of bichromate of potash.

A certain quantity of the substances to be examined is mixed with muriatic acid, solution of starch and iodide of potassium; the chromic solution is then added until the production of a blue colour :—

$$Cr^2O^6 + 3SO^2 = Cr^2O^3 + 3SO^3.$$

$$x = \frac{3SO^2 \cdot c \cdot C \cdot 100}{KO\,Cr^2O^3 \cdot A}.$$

One part by measure of a solution of sulphurous acid was tested with bichromate of potash, and an equal quantity of the same solution by Bunsen's method with solution of iodine :—

With bichromate of potash.	With iodine.
C=0·75	C=3·7
c=0·01	c=0·005
Found.	Found.
SO^2=0·02332	SO^2=0·02381.

From the examples here given it appears that this method possesses sufficient exactness to be employed, not only in technical, but also in scientific investigations.

In conclusion, it may be remarked, that it is probable that other bodies may be determined by this method, as, for instance, antimony and arsenic; but I have not yet been able to pay any attention to these substances.—*Ann. der Phys. und Chem.*, xcii. p. 57.

On the Separation of Tungstic Acid from Oxide of Tin.
By W. P. Dexter.

Both these metallic acids occur together in many tantalites, and their separation is attended with difficulty. The following process, recommended to me by Prof. H. Rose, succeeded perfectly in separating them.

Weighed quantities of oxide of tin and tungstic acid were heated to redness in a porcelain crucible, whilst a current of dry hydrogen gas was passed in through an opening in the cover. The loss of

weight was nearly as great as it would be if the oxide of tin had been completely reduced, and the tungstic acid converted into oxide of tungsten. The calcined mass was boiled with muriatic acid, and sulphuret of tin thrown down from the filtered solution by means of sulphuretted hydrogen; this was then converted into oxide of tin by careful roasting. The oxide of tungsten was converted into tungstic acid by heating to redness in the air.

0·392 grm. of oxide of tin and 0·452 grm. of tungstic acid lose, by calcination in an atmosphere of hydrogen, 0·109 grm. (from calculation they should lose 0·113 grm.). The quantity of oxide of tin recovered was 0·390 grm., and that of tungstic acid 0·446 grm. There were therefore—

	Employed.	Recovered.
Oxide of tin	46·44	46·21 per cent.
Tungstic acid	53·56	52·81 ...

Another method of separation, by fusion with bisulphate of potash, did not succeed. When the fused mass was treated with cold water, the washed oxide of tin still retained nearly a third of the tungstic acid employed.—Poggendorff's *Annalen*, xcii. p. 335.

PROCEEDINGS OF SOCIETIES.

Royal Society.

April 27, 1854. (The Earl of Rosse, President, in the Chair.)

"On the Changes produced in the Blood by the administration of Cod-liver Oil and Cocoa-nut Oil." By Theophilus Thompson, M.D., F.R.S.

The author has found that during the administration of cod-liver oil to phthisical patients their blood grew richer in red corpuscles, and he refers to a previous observation of Dr. Franz Simon to the same effect. The use of almond-oil and of olive-oil was not followed by any remedial effect, but from cocoa-nut oil results were obtained almost as decided as from the oil of the liver of the Cod, and the author believes it may turn out to be a useful substitute. The oil employed was a pure cocoa oleine, obtained by pressure from crude cocoa-nut oil, as expressed in Ceylon and the Malabar coast from the *Copperah* or dried cocoa-nut kernel, and refined by being treated with an alkali and then repeatedly washed with distilled water. It burns with a faint blue flame, showing a comparatively small proportion of carbon, and is undrying.

The analysis of the blood was conducted by Mr. Dugald Campbell. The whole quantity abstracted having been weighed, the coagulum was drained on bibulous paper for four or five hours, weighed and divided into two portions. One portion was weighed and then dried in a water-oven, to determine the water. The other was macerated in cold water until it became colourless, then moderately dried and digested with æther and alcohol to remove fat, and finally dried completely and weighed as fibrine. From the respective

weights of the fibrine and the dry clot that of the corpuscles was calculated. The following were the results observed in seven different individuals affected with phthisis in different stages of advancement:—

		Red corpuscles.	Fibrine.
First stage, before the use of cod-liver oil	Female	129·26	4·52
	Male	116·53	13·57
First stage, after the use of cod-liver oil	Female	136·47	5·00
	Male	141·53	4·70
Third stage, after the use of cod-liver oil	Male	138·74	2·23
Third stage, after the use of cocoa-nut oil.....	Male	139·95	2·31
	Male	144·94	4·61

June 15, 1854. (The Earl of Rosse, President, in the Chair.)

"On Osmotic Force." By Prof. Graham, V.P.R.S. (The Bakerian Lecture.)

This name was applied to the power by which liquids are impelled through moist membrane and other porous septa in experiments of endosmose and exosmose. It was shown that with a solution of salt on one side of the porous septum and pure water on the other side (the condition of the osmometer of Dutrochet when filled with a saline solution and immersed in water), the passage of the salt outward is entirely by diffusion, and that a thin membrane does not sensibly impede that molecular process. The movement is confined to the liquid salt particles, and does not influence the water holding them in solution, which is entirely passive: it requires no further explanation. The flow of water inwards, on the other hand, affects sensible masses of fluid, and is the only one of the movements which can be correctly described as a current. It is osmose, and the work of the osmotic force to be discussed.

As diffusion is always a double movement—while salt diffuses out, a certain quantity of water necessarily diffusing in at the same time in exchange—diffusibility might be imagined to be the osmotic force. But the water introduced into the osmometer in this way has always a definite relation to the quantity of salt which escapes, and can scarcely rise in any case above four or six times the weight of salt, while the water entering the osmometer often exceeds the salt leaving it, at least one hundred times. Diffusion is therefore quite insufficient to account for the water current.

The theory which refers osmose to capillarity appears to have no better foundation. The great inequality of ascension assumed among aqueous fluids is found not to exist, when their capillarity is correctly observed: and many of the saline solutions which give rise to the greatest osmose are undistinguishable in ascension from pure water itself.

Two series of experiments on osmose were described, the first series made with the use of porous mineral septa, and the second series with animal membrane. The earthenware osmometer con-

sisted of the porous cylinder employed in voltaic batteries, about 5 inches in depth, surmounted by an open glass tube 0·6 inch in diameter, attached to the mouth of the cylinder by means of a cap of gutta percha. In conducting an experiment the cylinder was filled with any saline solution to the base of the glass tube, and immediately placed in a large jar of distilled water; and as the fluid within the instrument rose in the tube, during the experiment, water was added to the jar so as to prevent inequality of hydrostatic pressure. The rise (or fall) of liquid in the tube was highly uniform, as observed from hour to hour, and the experiment was generally terminated in five hours. From experiments made on solutions of every variety of soluble substance, it appeared that the rise or osmose is quite insignificant with neutral organic substances in general, such as sugar, alcohol, urea, tannin, &c.; so also with neutral salts of the earths and ordinary metals, and with chlorides of sodium and potassium, nitrates of potash and soda and chloride of mercury. A more sensible but still very moderate osmose is exhibited by hydrochloric, nitric, acetic, sulphurous, citric and tartaric acids. These are surpassed by the stronger mineral acids, such as sulphuric and phosphoric acid and sulphate of potash, which are again exceeded by salts of potash and soda possessing either a decided acid or alkaline reaction, such as binoxalate of potash, phosphate of soda and carbonates of potash and soda. The highly osmotic substances were also found to act with most advantage in small proportions, producing in general the largest osmose in the proportion of one-quarter per cent. of salt dissolved. Osmose is eminently the phænomenon of weak solutions. The same substances are likewise always chemically active bodies, and possess affinities which enable them to act upon the material of the earthenware septum. Lime and alumina were accordingly always found in solution after osmose, and the corrosion of the septum appeared to be a necessary condition of the flow. Septa of other materials, such as pure carbonate of lime, gypsum, compressed charcoal and tanned sole-leather, although not deficient in porosity, gave no osmose, apparently because they are not acted upon chemically by the saline solutions. Capillarity alone was manifestly insufficient to produce the liquid movement, while the *vis motrix* appeared to be chemical action.

The electrical endosmose of Porrett, which has lately been defined with great clearness by Wiedemann, was believed to indicate the possession of a peculiar chemical constitution by water, while liquid, or at least the capacity to assume that constitution when polarized and acting chemically upon other substances. A large but variable number of atoms of water are associated together to form a liquid molecule of water, of which an individual atom of oxygen stands apart forming a negative or chlorous radical, while the whole remaining atoms together are constituted into a positive or basylous radical, which last will contain an unbalanced equivalent of hydrogen giving the molecule basicity, as in the great proportion of organic radicals. Now it is this voluminous basylous radical that travels in the electrical decomposition of pure water, and resolves itself into hydrogen

gas and water at the negative pole, causing the accumulation of water observed there, while the oxygen alone proceeds in the opposite direction to the positive pole. Attention was also called to the fact that acids, and alkalies, when in solution, are chemically combined with much water of hydration, sulphuric acid for instance evolving heat when the fiftieth equivalent of water is added to it. In the combination of such bodies, the disposal of the water is generally overlooked. Osmose was considered as depending upon such secondary results of combination, that is, upon the large number or voluminous proportions of the water molecules involved in such combinations. The porous septum is the means of bringing out and rendering visible, both in electrical and ordinary osmose, this liquid movement attending chemical combinations and decompositions.

Although the nature and *modus operandi* of chemical action producing osmose remains still very obscure, considerable light is thrown upon it in the application of septa of animal membrane. Ox-bladder was found to acquire greatly increased activity, and also to act with much greater regularity when first divested of its outer muscular coat. Cotton calico also impregnated with liquid albumen and afterwards exposed to heat so as to coagulate that substance, was sufficiently impervious, and formed an excellent septum, resembling membrane in every respect. The osmometer was of the usual bulb-form, but the membrane was supported by a plate of perforated zinc, and the instrument provided with a tube of considerable diameter. The diameter of the tube being one-tenth of that of the mouth of the bulb or the disc of membrane exposed to the fluids, a rise of liquid in the tube, amounting to 100 millimeters, indicated that as much water had permeated the membrane and entered the osmometer, as would cover the whole surface of the membrane to a depth of one millimeter, or one twenty-fifth part of an inch. Such millimeter divisions of the tube become degrees of osmose, which are of the same value in all instruments.

Osmose in membrane presented many points of similarity to that in earthenware. The membrane is constantly undergoing decomposition and its osmotic action is exhaustible. Salts and other substances, also capable of determining a large osmose, are all chemically active substances, while the great mass of neutral organic substances and perfectly neutral monobasic salts of the metals, such as chloride of sodium, possess only a low degree of action or are wholly inert. The active substances are also relatively most efficient in small proportions. When a solution of the proper kind is used, the osmose or passage of fluid proceeds with a velocity wholly unprecedented in such experiments. The rise of liquid in the tube with a solution containing one-tenth of a per cent. carbonate of potash in the osmometer, was 167 degrees, and with 1 per cent. of the same salt 206 degrees, in five hours. With another membrane and stronger solution, the rise was 863 millimeters, or upwards of 38 inches, in the same time, and as much water was therefore impelled through the membrane as would cover its whole surface to a depth of 8·6 millimeters or one-third of an inch. The chemical action must be

different on the substance of the membrane, at its inner and outer surfaces, to induce osmose; and according to the hypothetic view which accords best with the phænomena, the action on the two sides is not unequal in degree only, but also different in kind. It appears as an alkaline action on the albuminous substance of the membrane, at the inner surface, and as an acid action on the albumen at the outer surface. The most general empirical conclusion that can be drawn is, that the water always accumulates on the alkaline or basic side of the membrane. Hence, with an alkaline salt, such as carbonate or phosphate of soda in the osmometer, and water outside, the flow is inwards. With an acid in the osmometer, on the contrary, the flow is outwards, or there is negative osmose, the liquid then falling in the tube. In the last case the water outside is basic when compared with the acid within, and the flow is therefore still towards the base. The chloride of sodium, chloride of barium, chloride of magnesium, and similar neutral salts, are wholly indifferent, or appear only to act in a subordinate manner to some other active acid or basic substance, which last may be present in the solution or membrane only in the most minute quantity. Salts which admit of dividing into a basic subsalt and free acid exhibit an osmotic activity of the highest order. Such are the acetate and various other salts of alumina, iron and chromium, the protochloride of copper and tin, chloride of copper, nitrate of lead, &c. The acid travels outwards by diffusion, superinducing a basic condition of the inner surface of the membrane and an acid condition of the outer surface, the favourable condition for a high positive osmose. The bibasic salts of potash and soda, again, although strictly neutral in properties, such as the sulphate and tartrate of potash, begin to exhibit a positive osmose, in consequence, it may be presumed, of their possible resolution into an acid supersalt and free alkaline base.

The following Table exhibits the osmose of substances of all classes:—

Osmose of 1 *per cent. solutions in Membrane.*

	Degrees.		Degrees.
Oxalic acid	−148	Chloride of zinc	54
Hydrochloric acid (0·1 per c.)	− 92	Chloride of nickel	88
Terchloride of gold	− 54	Nitrate of lead	125 to 211
Bichloride of tin	− 46	Nitrate of cadmium	137
Bichloride of platinum	− 30	Nitrate of uranium	234 to 458
Chloride of magnesium	− 3	Nitrate of copper	204
Chloride of sodium	+ 2	Chloride of copper	351
Chloride of potassium	18	Protochloride of tin	289
Nitrate of soda	2	Protochloride of iron	435
Nitrate of silver	34	Chloride of mercury	121
Sulphate of potash	21 to 60	Protonitrate of mercury	356
Sulphate of magnesia	14	Pernitrate of mercury	476
Chloride of calcium	20	Acetate of sesquioxide of iron	194
Chloride of barium	21	Acetate of alumina	280 to 393
Chloride of strontium	26	Chloride of aluminium	540
Chloride of cobalt	26	Phosphate of soda	311
Chloride of manganese	34	Carbonate of potash	439

The osmotic action of carbonate of potash and other alkaline salts is interfered with in an extraordinary manner by the presence of chloride of sodium, being reduced almost to nothing by an equal proportion of that salt. The moderate positive osmose of sulphate of potash is converted into a very sensible negative osmose by the presence of the merest trace of a strong acid, while the positive osmose of the first-mentioned salt is singularly promoted by a small proportion of an alkaline carbonate. The last statement is illustrated by the following observations :—

Osmose in same membrane.

	Degrees.
1 per cent. sulphate of potash	21
Same +0·1 per c. carb. potash ..	254
Same + Same	264
0·1 per cent. carbonate of potash alone	92
Same	95

It may appear to some that the chemical character which has been assigned to osmose takes away from the physiological interest of the subject, in so far as the decomposition of the membrane may appear to them to be incompatible with vital conditions, and that osmotic movement must therefore be confined to dead matter. But such apprehensions are, it is believed, groundless, or at all events premature. All parts of living structures are allowed to be in a state of incessant change, of decomposition and renewal. The decomposition occurring in a living membrane, while effecting osmotic propulsion, may possibly therefore be of a reparable kind. In other respects chemical osmose appears to be an agency particularly adapted to take part in the animal œconomy. It is seen that osmose is peculiarly excited by dilute saline solutions, such as the animal juices really are, and that the alkaline or acid property which these juices always possess is another most favourable condition for their action on membrane. The natural excitation of osmose in the substance of the membranes or cell-walls dividing such solutions seems therefore almost inevitable.

In osmose there is further a remarkably direct substitution of one of the great forces of nature by its equivalent in another force—the conversion, as it may be said, of chemical affinity into mechanical power. Now what is more wanted in the theory of animal functions than a mechanism for obtaining motive power from chemical decomposition as it occurs in the tissues ? In minute microscopic cells, the osmotic movements should attain the highest velocity, being entirely dependent upon extent of surface. May it not be hoped, therefore, to find in the osmotic injection of fluids the deficient link, which certainly intervenes between muscular movement and chemical decomposition ?

THE CHEMICAL GAZETTE.

No. CCLXXXIII.—August 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Volatile Bases produced by Destructive Distillation of the Bituminous Shale of Dorsetshire. By C. Greville Williams.

Among the multitude of remarkable products with which organic chemistry has enriched science, there is perhaps no class of compounds which possess more points of interest, and hold out greater hopes of important applications, than the volatile organic bases. Their numerous metamorphoses, very singular constitution, and the many instances of isomerism to be found among them, are quite sufficient to make their history in the highest degree worthy of study, without considering the light which it has been hoped the decompositions attending their examination will throw on the grand problem of the artificial production of the cinchona alkaloids.

The researches of Anderson, Hofmann, and Stenhouse have shown it to be more than probable that all nitrogenous animal and vegetable matters yield volatile organic bases by destructive distillation; and, in the hands of the first-named chemist, bone-oil has been made to yield, not only a number of bases which have by some been considered characteristic of the decomposition of the gelatinous tissues, but also several of the alkaloids of the æthyle and methyle series discovered by Wurtz.

Proceeding upon these data, it was easy to foresee that the highly nitrogenous bituminous shale of Dorsetshire, so rich in semi-fossilized animal remains, would yield organic bases among the products of its destructive distillation; and it became therefore a problem of considerable interest to ascertain their nature and relation to those procurable by analogous processes from recent bones.

Not being in a position to distil the shale itself, and the Company's works having been abandoned, the only source of material for experiment became the thick red treacly matter which was produced by agitating the crude naphtha with oil of vitriol, in the process of purification, a quantity of which happened to be at my command.

To separate the tarry matters, the substance referred to was repeatedly boiled with water, which had the effect of resinifying the tar, and enabling it on cooling to be removed from the surface.

During the boiling, a large quantity of Runge's pyrrole was evolved, as shown by the extreme rapidity with which slips of fir-wood moistened with hydrochloric acid acquired an intense purplish-red colour when exposed to the steam.

When it was found that no more pitch was formed by boiling, the substance was evaporated to a small bulk, saturated with lime or potash, and distilled; the product was then supersaturated with hydrochloric acid, and the non-basic oil separated; the liquid, on being treated with an alkali and distilled as before, yielded the oily bases, containing a small quantity of ammonia, which was removed by washing with a strong solution of potash, in which they were almost insoluble. After this treatment, the only foreign body present was water, of which they contained about a third of their bulk, and which was separated by sticks of potash.

The entire absence of non-basic oils in the liquid thus procured was proved by its ready and complete solubility in hydrochloric acid; and that the ammonia was perfectly removed was evident from the ease with which their chlorides dissolved in absolute alcohol. In fact, the temperature at which they were rectified will be shown further on to be too high for ammonia to remain in them.

The liquid obtained by this process was placed in a retort with a thermometer in the tubulature; on heat being applied, ebullition commenced at 200° F., but did not become rapid until 260°; the mercury then rose quickly to 300°, at which point it was stationary for a few minutes; it then rose to 318°, between which point and 322° it was again steady for a short time, but soon commenced rising rapidly, and showed no further tendency to a fixed point.

It being therefore evident that the fluid under examination was a mixture of several bases of different boiling-points, it was resolved to subject it to a rigid fractionation, the receiver being changed at every 10 degrees, and each fraction thus obtained being again submitted to a similar treatment, that portion only being received as a rectified product which came over between the same points in several successive distillations. In this way upwards of a fortnight was expended before products could be obtained with boiling-points at all approaching to constancy; and it is worthy of remark, that whereas at first only a very minute fraction could be obtained below 320°, after about half a dozen rectifications the product below that point was more in quantity than the united bulk of all the rest of the fractions.

The bases thus obtained are limpid, colourless, highly refractive liquids, having a very singular and persistent odour, adhering strongly to the hands and clothes, and being far more pungent and disagreeable in the lower than the upper fractions; moreover, when the vapour of the former is inspired, the peculiar bitter of picoline is perceived. When the smell of the bases has been on the hands or clothes for some time, it becomes like that of soot.

The fractions burn with a brilliant but smoky flame, and they fume strongly on the approach of a rod wetted with hydrochloric acid.

They dissolve readily in acids with considerable elevation of temperature, and form crystallizable deliquescent salts. They all dissolve readily in alcohol and æther; they precipitate nitrate of copper, and in excess redissolve the precipitate, with production of a fine

blue colour; but the reaction is less rapid, and the colour less brilliant, than when ammonia is used.

They absorb carbonic acid, though slowly, the lower fractions doing so more energetically than the higher ones; and, in fact, the intensity of their action may in all cases be said to be inversely as the temperature at which they distil.

They may be divided into two groups by the difference in their solubility, those below 320° dissolving easily in water, and those distilling above that temperature being much less soluble, the insolubility increasing rapidly with the rise of boiling-point.

All the fractions form double salts with bichloride of platinum; those of the lower fractions crystallize with facility; the higher ones, on the contrary, with considerable difficulty.

All the products above 330° strike a yellow colour with fir-wood and hydrochloric acid. Those between 360° and 410° give, when treated with solution of bleaching powder, a beautiful green colour, which is due to the presence in small quantity of a base not yet isolated, to which I have given the name of *Vertidine*. At my request Dr. Anderson examined the fraction about that point from Dippel's oil, but could not ascertain the presence of vertidine; but on converting the portion coming over about 355° into a nitrate, and boiling with nitric acid until the aniline was completely destroyed, and then distilling with lime, he obtained a base which gave a feeble green tint with bleaching powder, and otherwise agrees in its general properties with vertidine. Whatever the nature of this base may prove to be, it evidently approximates closely in composition to those which distilled about 410°, since the fraction at that point has precisely the composition of lutidine.

It was attempted to isolate that base by repeated fractionation; but after an immense number of distillations, the base which afforded the green reaction was found to be too small in quantity to afford a chance of fixing it within a moderate range of degrees.

The first fraction obtained was between 200° and 210° F.; the quantity was so small that it was impossible to submit it to so complete a rectification as could have been wished; it was therefore saturated with hydrochloric acid, and bichloride of platinum added in excess. The crystals, which soon precipitated, filtered off, well washed with æther, and dried at 212° F., gave on combustion the following numbers:—

Carbon	23·96	..	12 =	72	24·07
Hydrogen	2·70	..	8	8	2·67
Nitrogen	..	..	1	14	4·73
Chlorine.....	..	..	3	106·5	35·59
Platinum	33·35	33·56	1	98·8	32·94

The base therefore is picoline, with the theoretical constitution of which the analysis almost exactly agrees. The true boiling-point of picoline is 272°; it would therefore appear strange to find it in a fraction collected at 210°, if we did not know how greatly boiling-points are modified by even a slight admixture of substances which

distil at different temperatures; besides which, the history of the boiling-points of these bases is full of anomalies: for instance, aniline, which has absolutely the same composition and atomic weight as picoline, boils 88° above that substance, namely at 360°; and it is singular that the same difference is found between the isomers lutidine and toluidine, the former boiling at 300° and the latter at 388°.

In fact, the volatile organic bases appear to present more remarkable cases of isomerism than any other class of substances: this will immediately be seen by reference to the highly singular and interesting alkaloids discovered by Dr. Hofmann.

The next fraction analysed was that coming over between 270° and 280°; it was converted into platinum salt and crystallized, the first crop only being used. After drying at 212°, it was burnt, and gave the following result:—

Carbon	26·14	14 =	84	26·81
Hydrogen	3·16	10	10	3·19
Nitrogen	..	1	14	4·49
Chlorine	..	3	106·5	34·00
Platinum	31·76	1	98·7	31·51

Dr. Anderson obtained, as a mean result of his analyses of platinochloride of lutidine from bone-oil,—

Carbon	26·35
Hydrogen	3·23
Nitrogen	..
Chlorine	..
Platinum	31·50

The numbers given above therefore agree pretty closely with the theoretical constitution of this base, which was discovered by Dr. Anderson among the alkaloids of Dippel's oil, and which, it is believed, has not, until the present time, been observed by any other chemist.

The deficiency in the carbon points to an admixture with picoline, which supposition is to some extent confirmed by the slight excess of platinum. To render this result the more certain, the mother-liquor, from which the crystals analysed were deposited, was evaporated and set aside, when a second crop was formed, which on careful ignition gave the following numbers:—

I.	II.	Theory (picoline).
32·76	32·83	32·94

We therefore see at once that the fraction between 270° and 280° consisted, even after repeated rectifications, of a mixture of the two bases, the first crop consisting chiefly of lutidine, and the second of picoline. This result, and many others obtained in the course of the investigation, show that the fractional crystallization of the platinum-salts of these bodies would be a far more accurate means of separation than distillation; in fact, Dr. Anderson states that he was only deterred from adopting this method by the very large quantity of

platinum necessary for the purpose. Moreover, it would avoid the great loss which is inevitably incurred in so many distillations, which arises, not only from the impossibility of condensing the whole of the vapour in an apparatus which has to be taken to pieces every few minutes, but also from the fact that the bases are partially decomposed by exposure to a high temperature, a perfectly colourless distillate becoming brown after boiling for some time.

The next fraction which was analysed was that which came over between 300° and 310°: it had a somewhat less pungent and more aromatic odour than the previous products. It was analysed by passing its vapour over oxide of copper, the usual precautions being taken in all the analyses to prevent the oxidation of the nitrogen from rendering the carbon determination inaccurate:—

Carbon	78·83	78·55	14 = 84	78·50
Hydrogen	8·50	8·60	9	8·41
Nitrogen	12·68	12·85	1	14	13·09

These analyses therefore agree almost exactly with the theoretical composition of lutidine; and, moreover, the base came over at the temperature which has been assigned to lutidine as its boiling-point by the discoverer.

With the intention of confirming the result of the analysis, a determination was made of the platinum in the double salt of that metal, with the following result:—

	I.	II.	Theory.
Platinum ...	31·51	31·82	31·51

Carmidine.—By passing the vapour of the last fraction (lutidine) over red-hot lime, it is decomposed, with deposition of carbon, the lime becoming black to the centre of the fragments, and what appears to be a new base is formed, to which the above name may be given. Its reactions are, perhaps, more marked than any of the volatile bases of this class yet known. With fir-wood and muriatic acid a beautiful red tint is produced, and with bleaching powder a fine bluish-green, of a different tint and developed in a different manner from that obtained with the same reagent from vertidine, the new base which has been alluded to previously, the colour commencing from the top of the liquid, whereas in vertidine it begins from the bottom. The tint is moreover much less fugitive than that of the other base. Several attempts were made to isolate it, but the very small quantity at my disposal was exhausted before the experiments were sufficiently advanced to enable me to procure it in a state fit for analysis. Unfortunately the platinum salt as at present procured does not crystallize, but forms a mass of the consistence of Venice turpentine, exceedingly soluble in water and spirit, from a solution in which it is precipitated by æther in the state of oily drops. Results have been obtained which indicate that the mercury salt will afford the means of ascertaining its constitution. It is possible that the reactions of carmidine may arise from the conversion of a portion of the lutidine into pyrrole and vertidine; and the difference in the manner in which the green colour is developed may be caused

by the presence of some impurity at present unknown: the subject is now under investigation.

The next fraction examined was that between 350° and 360°:—

	I.	II.	Theory.
Carbon	78·54	78·77	78·50
Hydrogen	8·64	9·09	8·41
Nitrogen	12·82	12·15	13·09

being the same result as the last analysis. The specific gravity of this fraction was 0·928.

The next distillate analysed after this, came over between 380° and 440°, the rise of the thermometer being too rapid to allow of intermediate fractions being obtained. It furnished:—

Carbon.....	78·75
Hydrogen	8·92
Nitrogen	12·34

the per-centage composition of lutidine being still indicated, with however a sufficient rise in the carbon and hydrogen to show an admixture of the next base. It is submitted that these last results are important, as showing how greatly the boiling-points of this class of bodies are influenced by the presence of bases of closely approximating constitution, but which distil at a higher temperature. It has been shown by Anderson, in his investigation of the Dippel's oil bases, that fractions obtained at considerable thermometric intervals may have almost exactly the same composition under the circumstances just indicated. In his analysis of the same base, he made use of fractions from 310° to 324°, and in the platinum salts from 295° to 335°.

There is no doubt, however, that if sufficient material had been at my disposal, so as to allow of a more perfect separation by fractional distillation, the base of the composition found in the last four fractions might have been brought much closer to its real boiling-point, and not have extended over so very large a range of degrees as from 300° to 440°. After the distillations had been repeated a great number of times, the chief bulk was condensed into a few degrees on each side of 310°; the fractions therefore after 340° were exceedingly small in quantity, which rendered their further purification by this method impracticable.

The next fraction analysed was that coming over between 440° and 460°:—

Carbon	79·34	16	= 96	79·33
Hydrogen	9·12	11	11	9·09
Nitrogen.....	11·55	1	14	11·58

being exactly the composition of the base of the picoline series next to lutidine, the discovery of which in bone-oil was communicated to me by Dr. Anderson about a fortnight previous to its being found among the products of the distillation of the Dorsetshire shale. It is believed that no account of it has yet been published. The boiling-point was found by Anderson to be about 355: this discre-

pancy is easily accounted for, the quantity at my disposal being too small to allow of its being separated perfectly from the next base, which has probably a boiling-point of 500°, a small quantity of liquid remaining in the retort at that temperature.

The next fraction that was obtained in sufficient quantity for analysis came over between 460° and 490°:—

Carbon	79·43
Hydrogen	8·87
Nitrogen	11·70

This result is too close to the last to allow of our deriving a different formula from it; but there is still another fraction which does not volatilize when the thermometer has risen to 500°, though in too minute a quantity for an accurate examination*; as, however, it was not probable that I should have an opportunity, for a long time, of obtaining the material for another investigation, I was most desirous of pushing the inquiry as far as possible, in the endeavour to demonstrate the presence of the next base of the series, which would be isomeric with cumidine. The first experiment showed me that I was not to expect rigorously accurate results, for that a partial decomposition had taken place was evident from the fact, that, although the substance when first prepared, about two months previously, did not contain a trace of water, nevertheless, on redistillation, the first portion contained a little of that substance.

The quantity being insufficient for purification, it was introduced into a very small retort, blown on a piece of tube, and brought over very slowly, the product being received in four portions containing about ten drops in each. The first fraction was rejected, as it contained the chief part of the water: the other three were burnt, with the following results:—

Carbon	81·04	80·23	80·85	18	80·00
Hydrogen	9·21	8·89	8·28	13	9·62
Nitrogen	9·75	10·88	10·87	1	10·38

The decomposition which had taken place having acted by removing the hydrogen in the form of water, and also by eliminating some substance or substances containing excess of carbon, as shown by the dark colour of the distillate, renders the very considerable difference between the theoretical and experimental numbers easy of explanation; in fact, it is remarkable that the difference is not greater, especially when it is considered that the circumstances detailed rendered further purification impossible.

Some peculiarities in the character of this base having rendered its history worthy of some examination, I have promised myself to return to the subject as soon as I have obtained a further supply of material; in the meantime I propose to assign it the name of *Parvoline*, in allusion to its small volatility as compared with its associated bases.

If the analyses just given were the only proofs obtainable, I

* Somewhat less than a drachm was obtained.

should be diffident in quoting them as decisive evidence of the presence of a new base; but taken in conjunction with the other phænomena observed in the course of the investigation, and especially with the fact of the steady increase in the carbon and hydrogen in the previous fractions, it is submitted that there can be no doubt whatever of the existence in shale-naphtha of the isomer of cumidine, in which case we have five members of a group of the general formula $(C^n H^{n-5}) N$, of which the following terms are known:—

Pyridine	$C^{10} H^5 N$
Picoline	$C^{12} H^7 N$
Lutidine	$C^{14} H^9 N$
Anderson's new base	$C^{16} H^{11} N$
Parvoline	$C^{18} H^{13} N$

It will be seen that the carbon and hydrogen advance by steps of $C^2 H^2$, and that the carbon is always 5 equivs. more than the hydrogen.

It is hoped that this fact, and an examination of their products of decomposition, will soon enlighten us as to their constitution. In a communication recently received from Dr. Anderson, he states that he has discovered picoline to be a nitryle base, which becomes the more remarkable when we consider that the members of this class contain three radicals; and there being in this instance only 7 equivs. of hydrogen to divide between the three, their constitution must be extremely singular. This is still more evident in the case of pyridine, where 5 equivs. of hydrogen have to be divided into three groups. We may probably expect from the labours of Dr. Anderson, with which he is at present engaged, a complete history of the properties and constitution of these remarkable bodies.

It is highly interesting to observe the strict parallelism which exists between the two groups of bases, of which aniline forms the first term in the one case, and pyridine in the other. For example,—

Unknown	$C^{10} H^5 N$	Pyridine	$C^{10} H^5 N$
Aniline	$C^{12} H^7 N$	Picoline	$C^{12} H^7 N$
Toluidine	$C^{14} H^9 N$	Lutidine	$C^{14} H^9 N$
Xylidine*	$C^{16} H^{11} N$	New base	$C^{16} H^{11} N$
Cumidine	$C^{18} H^{13} N$	Parvoline	$C^{18} H^{13} N$

One of the aniline series is seen to be wanting, namely, the isomer of pyridine; this term might doubtless be supplied by treating its corresponding hydrocarbon in the same way that aniline is obtained from benzole, cumidine from cumole, &c.†

* Comptes Rendus, vol. xxx. p. 319.

† While on this track, I subjected the more volatile portion of coal-tar naphtha to a careful fractionation, and obtained a very small quantity of a product boiling at 110°, which was acted on by nitric acid; but the compound dissolved almost entirely in the large quantity of water into which it was thrown, with the intention of precipitating it, and from which I was unable to separate it in a state fit for the action of sulphuretted hydrogen: this, however, is not a serious difficulty, and I hope very soon to obtain a more satisfactory result.

It is somewhat singular, that while aniline is at present the type of the one series, that it is nevertheless found among the bases of Dippel's oil associated with the picoline group, and yet that the latter class, as obtained from the shale products, does not contain a trace of aniline. Stenhouse also demonstrated its absence from the bases obtained by him from beans. It is evident also that the last-named chemist's bases have many points of resemblance to those from bones and the Dorsetshire shale: in fact, the formula which he deduces from the analyses of the fraction between 302° and 311° only differs from the constitution of pyridine by 1 equiv. of hydrogen, and the carbon in the portion distilling between 392° and 410° is almost exactly the theoretical amount in that base. The hydrogen, on the other hand, approaches closely to the per-centage in lutidine.

In a specimen of the base from beans, which I was shown by Dr. Stenhouse, I observed the peculiar bitter sensation, on inhaling its vapour, which has been previously alluded to as characteristic of picoline: it becomes, therefore, extremely probable that the bean bases are mixtures of those found in the Dippel's oil and shale products, with some substance easily decomposed and resinified by nitric acid.

It results, in effect, from the experiments detailed, that the bituminous shale yields by its distillation several bases, which are identical with those procured by the same processes both from coal and also from recent bones; but although this is the case, we cannot but be surprised at the absence of aniline, which from its marked reactions had become to a certain extent characteristic of this class of decomposition.

In conclusion, it is suggested, that as in the present state of our knowledge pyridine forms the first step of the one class, it would be more regular to give its name to the group, instead of calling it the "Picoline Series," as is usually done.—From the *Quarterly Journal of the Chemical Society* for July, 1854.

On the Preparation of some Compounds of Sulphur. *By* Skoblikoff.

The author states that he, in conjunction with Radloff, has prepared sulphuret of boron by treatment of borates with sulphuretted hydrogen. He has also obtained several metallic sulphurets in the same way.—*Bull. de St. Pétersb. Cl. Math.-Phys.*, xii. p. 319.

On the Conjugate Ureas. *By* Dr. N. Zinin.

Chloride of benzoyle only acts upon urea with difficulty; but this compound (*benzureid*), as well as other conjugate ureas, is obtained by treating urea, under certain conditions, with the chlorides of the radicals (chloracidyles). The author has prepared these ureas with the chloracidyles of the monobasic acids.

Benzureid, $C^{16}H^8N^2O^4 = C^2N^2(H^3.C^{14}H^5O^2)O^2$.—This compound is obtained by pouring 1 equiv. of chloride of benzoyle over

2 equivs. of dry pounded urea, and heating in an oil-bath to 302°–311° F., when the urea fuses beneath the chloracidyle. As soon as no more crystals of urea are to be felt with a glass rod, the vessel is removed from the bath and its contents stirred briskly round. The urea then mixes with the chloride of benzoyle; the temperature of the mixture rises, it becomes thicker, and acquires the consistence of a soft tough paste, separating from the sides of the vessel. Care must however be taken that the temperature does not rise far above 320° F., which may even take place during the stirring with the glass rod; it is also advisable not to operate upon too great quantities of material at once, but to employ at the outside 12 to 15 grms. of urea. The reaction is completed when the mass is capable of being worked up into a lump; the odour of chloride of benzoyle has then completely disappeared, but if the temperature has not been sufficiently regulated, a faint odour of benzonitryle often occurs. When perfectly cold, the mass is tolerably hard; its weight nearly equals that of the materials employed (30 grms. of mixture rarely lose more than 0·750 grm.); and when treated with æther, it communicates an acid reaction to that fluid, but loses scarcely anything in weight. When the triturated mass is treated with cold alcohol, it loses about one-third of its weight, the alcohol acquires a strongly acid reaction, and contains muriatic acid and urea.

The mass remaining after washing with strong alcohol constitutes a crystalline powder, the solution of which in boiling alcohol deposits on cooling long, thin, four-sided, often pointed laminæ, which cohere into groups. These crystals are of a white colour and strong lustre, resembling benzoic acid in appearance; they are however difficult of solution in alcohol, as 1 part requires 24 parts of boiling, and nearly 100 parts of cold alcohol for its solution. These crystals are still more difficult of solution in water, whether cold or boiling, and in æther. When dissolved in hot, tolerably strong muriatic acid, which dissolves it in greater quantity than water, the substance recrystallizes unchanged; nitric acid decomposes it when heated, and crystals of benzoic acid separate from the solution. It is not attacked by ammonia; cold solution of potash dissolves it readily, and from this solution, even when gently heated, acids throw down the substance unchanged. But when this solution is boiled, ammonia is evolved, and a mixture of carbonate and benzoate of potash remains. When heated on platinum foil, it fuses, and at first evolves an odour of benzonitryle; it is afterwards completely volatilized, whilst at last the odour of cyanic acid is recognizable. When heated in a tube to 392° F., it fuses into a colourless fluid, which solidifies on cooling in a crystalline form; during this process the weight of the body remains unaltered, whilst its properties undergo a change, for the solidified mass dissolves more readily than benzureid, and crystallizes in a different form.

The further action of heat upon this body is interesting; it is the same with all the other ureids here described, with this distinction, that the decomposition is more easily effected with benzureid than with those ureids which contain groups of acids homologous with

formic acid. Thus if benzureid be heated a few degrees above its melting-point, the fluid begins to froth, and suddenly becomes filled with long white needles. If the mixture produced be now cooled and treated with hot alcohol, this extracts benzamide, and the acicular crystals, which consist of nothing but cyanuric acid, remain undissolved in the alcohol. The decomposition of 1 grm. of benzureid in the manner above described gave 0·250 cyanuric acid and 0·730 benzamide; it is therefore a true splitting, expressed by the following equation:—

$$3(C^2N^2[H^3.C^{14}H^5O^2]O^2)=C^6N^3H^3O^6, 3(N[H^2.C^{14}H^5O^2]).$$

Potash acts upon this body in the manner expressed in the following equation:—

$$C^2N^2(H^3, C^{14}H^5O^2)O^2, 3KHO^2=C^2K^2O^6+C^{14}H^5KO^4, 2NH^3.$$

Analysis:—

Carbon	58·68	16 =	96	58·53
Hydrogen	4·97	8	8	4·87
Nitrogen.....	16·38	2	28	17·07
Oxygen	19·97	4	32	19·53

Acetureid, $C^6H^6N^2O^4=C^2N^2(H^3.C^4H^3O^2)O^2$, is best obtained by allowing 1 equiv. of chloride of acetyle to act upon 2 equivs. of urea. It forms long four-sided needles, with a right-angled parallelogrammic base; these crystals are generally striated in the direction of their length, and have hollows, or four-sided longitudinal furrows, on one of the broadest surfaces. The colour of the body is a silky white; in its external appearance it resembles urea. 1 part of it required 10 parts of boiling alcohol for its solution; on its recrystallization from the cold solution, only about 1 part in 100 remained dissolved. It dissolves in hot water more readily than in alcohol; but on cooling, nearly the whole of the dissolved portion separates in the form of six- and four-sided prisms with rhombic bases and dihedric apices, arranged in plumose and stellate groups.

When acetureid is heated on platinum foil, a white vapour is evolved, and the crystals become covered with a woolly coating; when more strongly heated, it is all volatilized without residue. When heated in a tube, the formation of the woolly coat is observed at 320° F., but very little of it is formed even when the heat is raised to 392° F., at which temperature the substance fuses into a clear fluid. On cooling, this solidifies into a crystalline mass, which dissolves in water and alcohol; the alcoholic solution gives crystalline druses, composed of short, rather thick, pointed, rhombic prisms. By the further application of a continued, but not too strong heat, the same phænomenon is produced as with benzureid, namely, the resolution of the substance into acicular crystals of cyanuric acid and acetamide, the latter of which, at the high temperature at which it is produced, remains partly in the fluid form mixed with the crystals of cyanuric acid, and partly deposited on the cool sides of the vessel in the form of a woolly acicular coating. The quantity of cyanuric acid obtained agreed with the equation,—

$$3.(C^2N^2[H^3.C^4H^3O^2]O^2)=C^6N^3H^3O^6, 3.N[H^2.C^4H^3O^2].$$

The reaction with solution of potash is the same as with benzureid; the final decomposition in the hot solution is expressed by the following equation:—

$C^2N^2[H^3.C^4H^3O^2]O^2, 3KHO^2 = C^2K^2O^6, C^4.H^3K.O^4, 2NH^3.$

Analysis:—

Carbon	35·56	6 =	36	35·29
Hydrogen	5·92	6	6	5·88
Nitrogen	27·05	2	28	27·45
Oxygen	31·47	4	32	31·38

Bull. de St. Pétersb., Cl. Phys.-math., xii. p. 281.

On Hydrargyræthyle and its Compounds. *By* F. Dünhaupt.

Frankland obtained the iodine compound of hydrargyromethyle by the action of iodide of methyle upon mercury when exposed to the light of the sun. Hydrargyræthyle is not produced in the same way. The author readily obtained the compound of mercury and æthyle, by treating bismæthyle with chloride of mercury, as stated in a previous memoir*. The author prepared the following compounds of this base.

Chloride of Hydrargyræthyle, $(Hg^2Ae)Cl$, crystallizes in beautiful laminæ of a silvery lustre; it is soluble with difficulty in cold alcohol, but dissolves plentifully in this fluid when boiling; æther dissolves it in but small quantity, and it is almost insoluble in water. It sublimes at a very low temperature (at about 104° F.) in beautiful thin laminæ, without previous fusion; it volatilizes even when merely left in the air; when heated on the water-bath, it fuses into a clear oily fluid, and evaporates without leaving a trace of residue. Heated on platinum foil, it burns with a weak flame, diffusing a peculiar unpleasant odour. Analysis:—

Mercury	76·23	..	..	..	..	2 =	200·0	75·63
Carbon	8·73	8·87	9·02	9·62	9·39	4	24·0	9·06
Hydrogen	1·45	1·87	1·93	1·94	2·00	5	5·0	1·90
Chlorine	13·75	13·60	..	..	..	1	35·5	13·41

Bromide of Hydrargyræthyle, $(Hg^2Ae)Br$, is obtained either by adding to an alcoholic solution of bistriæthyle an alcoholic solution of bromide of mercury, or by mixing directly hydrated oxide of hydrargyræthyle with hydrobromic acid, or by adding an alcoholic solution of bromine to a similar solution of hydrated oxide of hydrargyræthyle as long as the colour of the former solution disappears; in the latter case bromate of hydrargyræthyle is formed at the same time. Bromide of hydrargyræthyle agrees very closely in its properties with the chloride. Analysis:—

Mercury	..	2 =	200	64·72
Æthyle	..	1	29	9·39
Bromine	25·84	1	80	25·89

* See Chem. Gaz., 1854, No. 282, p. 263.

Iodide of Hydrargyræthyle, (Hg^2 Ae) I, is obtained by mixing an alcoholic solution of hydrated oxide of hydrargyræthyle with an alcoholic solution of iodine as long as the colour of the latter disappears. If the solutions be employed warm and diluted, the iodide separates during cooling in remarkably beautiful, white, laminar crystals. After a considerable time, however, they acquire a slightly yellowish colour. This compound volatilizes completely without decomposition. Analysis:—

Mercury		2 =	200	56·20
Æthyle		1	29	8·15
Iodine	36·18	1	127	35·65

Sulphuret of Hydrargyræthyle, (Hg^2 Ae) S.—If sulphuret of ammonium be added to an alcoholic solution of chloride of hydrargyræthyle, a yellowish-white pulverulent precipitate of sulphuret of hydrargyræthyle is produced; an excess of sulphuret of ammonium must be avoided, as the compound is readily soluble in it; a great portion of it remains dissolved in the alcohol, in which it is also very soluble; æther also dissolves it readily. If the alcoholic solution be evaporated, the compound soon begins to decompose, with separation of sulphuret of mercury. After the evaporation of the ætherial solution, the compound is obtained in a crystalline form, although a slight separation of sulphuret of mercury always takes place. Analysis:—

Mercury	81·05	2 =	200	81·63
Carbon	8·95	4	24	9·79
Hydrogen	1·96	5	5	2·05
Sulphur	6·10	1	16	6·53

Cyanide of Hydrargyræthyle, (Hg^2 Ae) Cy (?).—When an alcoholic solution of bistriæthyle is added to an alcoholic solution of cyanide of mercury, the fluid remains perfectly clear, at the same time that a peculiar repulsive odour is evolved by it; but the separation of a yellowish-white powder soon commences, and continues for a considerable time. If it be filtered, the fluid still possesses a penetrating odour; but when it is evaporated, pure cyanide of mercury remains. The powder first separated is hydrated oxide of bismuth, to which a small quantity of oxide of bisæthyle still adheres. But if, on the contrary, the alcoholic solution of hydrated oxide of hydrargyræthyle be saturated with strong hydrocyanic acid, the cyanide is very readily produced, and separates in the course of a short time in a crystalline form. In its facility of crystallization this compound almost exceeds even the corresponding chlorine and bromine compounds; it is very volatile, and when heated in a glass tube evolves an exceedingly repulsive odour, which attacks the respiratory organs very strongly, and appears to be highly poisonous. Its products of decomposition are probably of a peculiar nature; when heated in the glass tube, a carbonaceous body remains. It is readily soluble in alcohol and æther.

Hydrated Oxide of Hydrargyræthyle, (Hg^2 Ae) O, HO.—This

compound is obtained by dissolving chloride of hydrargyræthyle in boiling alcohol, and shaking this solution with freshly-precipitated hydrated oxide of silver which has been washed with alcohol; the hydrated oxide of hydrargyræthyle remains dissolved in the alcohol; it is separated from the precipitated chloride of silver by filtration. The alcohol is now almost entirely distilled off by the water-bath, and the fluid remaining in the retort is put under the bell-glass of the air-pump over sulphuric acid. In a few days the pure hydrated oxide of hydrargyræthyle is left in the form of a nearly colourless, oily fluid; it has exactly the appearance of a fatty oil, and possesses no remarkable odour; it is very easily soluble in water and alcohol, and possesses strong basic properties. It feels slippery between the fingers, like hydrate of potash, and possesses an extremely caustic taste. When left for some time in contact with the skin, it produces a continuous violent burn, with blisters on the skin, like those produced by cantharides.

This base immediately separates ammonia from its compounds; if it be added to a solution of muriate of ammonia, it produces an instantaneous evolution of ammonia, especially when heated, and a glass rod moistened with weak muriatic acid held over it immediately produces white clouds; in a short time chloride of hydrargyræthyle crystallizes from the solution. Potash and magnesia are not separated by it from their solutions. The addition of the base to a solution of sulphate of alumina and potash immediately produced a voluminous precipitate of hydrated alumina.

When brought into contact with metallic zinc, the latter is amalgamated, and the fluid contains zincæthyle. If chloride of hydrargyræthyle be employed in this experiment, the fluid contains chloride of zincæthyle, which when heated upon platinum foil is decomposed, with formation of a strong white vapour; the residue is a mixture of carbon and oxide of zinc. With sulphate of zinc the base produces a white precipitate of hydrated oxide of zinc.

Sulphate of copper when heated gives a greenish-gray precipitate. In perchloride of iron the base produces a pale yellow flocculent precipitate, which is insoluble in an excess of perchloride of iron; when heated it is further decomposed, and acquires a reddish-brown colour. With protochloride of tin it gives a voluminous white precipitate. Perchloride of gold gives a yellow precipitate; when heated for a considerable time, gold separates in the form of a brown powder.

With chloride of platinum the base produces a yellowish-white precipitate, which dissolves very readily when heated; on cooling, a large quantity of crystalline laminæ separates, whilst the supernatant fluid remains perfectly clear. It is only by long-continued application of heat that decomposition is induced, when a black powder separates. It appears as though a double salt was formed in this case, but further investigations are necessary to decide this point.

If a great excess of sulphuretted hydrogen be added to the base, a white precipitate is formed, which after long standing becomes yellow, then brown, and at length black.

Oxide of hydrargyræthyle forms with nitric acid the salt $(Hg^2Ae)O, NO^5$, with phosphoric acid the salt $(Hg^2 Ae)O, PO^5$, with sulphuric acid the salt $(Hg^2 Ae)O, SO^3$. The carbonate, oxalate, and acetate of hydrargyræthyle are all crystallizable; the carbonate crystallizes with most difficulty. This salt was obtained by the decomposition of chloride of hydrargyræthyle by carbonate of silver at a gentle heat; after the separation of the chloride of silver, a considerable quantity of oxide of silver was always contained dissolved in the filtrate, and the pure salt could only be obtained by repeated evaporation and filtration. It crystallizes with difficulty; long-continued evaporation at 122° F. leaves a syrupous mass, which dissolves readily in water and alcohol, and evolves carbonic acid gas immediately on the addition of strong acids.—*The Author's Inaugural Dissertation*, Breslau, 1854.

On the Preparation of the Anhydrous Organic Acids.
By Dr. G. Wunder.

In experiments on the preparation of the anhydrous organic acids according to Gerhardt's directions, the author has found that, instead of oxychloride of phosphorus, the chloride PCl^5 may be employed. 1 equiv. of chloride of phosphorus was mixed with 6 equivs. of dry benzoate of soda, when the whole fused together from the heat produced by the reaction. Some time afterwards it was heated to 266° F.; the cooled mass was extracted with water, and the residue dissolved in boiling alcohol; from this, crystallized anhydrous benzoic acid was obtained. The analytical results agreed with the formula $C^{14} H^5 O^3$.—*Journ. für Prakt. Chem.*, lxi. p. 498.

ANALYTICAL CHEMISTRY.

On the Detection of Alcohol in Judicial Investigations.
By Dr. Ed. Strauch.

Thomson has recommended the use of chromic acid for the detection of alcohol. The author confirms the distinctness of the reaction by reduction, formation of aldehyde, &c., but points out the inaccuracies which may arise from the reduction being also caused by many other bodies, although these affect less the distillate.

The essential portion of the author's communication is the following description of a method of determining alcohol by means of platinum-black, which enables us to decide within a quarter to half an hour whether the distillate of the substance under examination for alcohol contains that body or not.

The part of the body to be examined for alcohol is to be finely divided immediately after it has been taken out of the corpse; or if the test cannot be immediately applied, it must be placed in a well-closed vessel, in order to prevent the volatilization of any alcohol

that may be contained in it. If the substance under investigation have an acid reaction, a few drops of very dilute solution of potash are carefully added to it until a piece of litmus-paper dipped into the mixture is no longer reddened. The substance is then put into a tubulated retort, either by means of a funnel or a pair of forceps. This may be of such a size as to hold about 1 lb. of water. For smaller quantities smaller retorts may be made use of, but it is always well to use as much as possible of the substance to be tested. If it be desired to detect alcohol in the lungs, the retort must only be half-filled, as the lungs when heated froth up very much, and by this means a portion of the mass in the retort may boil over. The retort is placed in a water-bath, and so arranged that its neck may be but little bent down. This is broken off so far up that a tray of platinum, fine silver or glass, of about $\frac{1}{3}$rd of an inch in breadth and 2 inches long, may be slipped into it. Into this tray some platinum-black is put, and at each end of it is placed a piece of blue litmus-paper moistened with distilled water, which must be partially in contact with the platinum-black. The tray is now pushed, by means of a wire hook, to the place where the neck of the retort passes into its belly, and the water-bath is heated by means of a spirit-lamp. The operation may be facilitated by filling the water-bath with a solution of chloride of calcium or sodium, instead of water. As alcohol boils at a lower temperature than water, it of course is the first to be driven off. As soon therefore as the first water-drops begin to condense in the neck of the retort, that portion of the litmus-paper which is in contact with the platinum-black becomes reddened, whilst that portion which is turned towards the belly of the retort still remains blue, and thus at once shows that the acid did not come out of the retort, but was only formed in contact with the platinum-black. When the heat has been applied for some time, and single drops begin to run from the neck of the retort, without any reddening of the litmus-paper, we may conclude with certainty that no trace of alcohol was contained in the substance under examination. But if, on the contrary, the litmus-paper is quickly and strongly reddened, and it be desired to produce further proof of the presence of alcohol, the tray is again to be drawn out of the neck of the retort; the latter is then bent down a little more, a receiver is attached to it, and distillation is continued until the distillate amounts to several drachms, during which the receiver is cooled by a cloth soaked with cold water. The distillate is then transferred into a small retort, and about the same quantity of fused chloride of calcium; or if this be not at hand, well-dried chloride of sodium is added to it. This retort is then put upon the water-bath in pure water, a receiver is attached to it, and distillation continued as long as anything passes over. A few drops of this second distillate may now be added to a mixture of bichromate of potash and sulphuric acid, to obtain the alcohol reaction. The remainder of the distillate may be made use of to ascertain the specific gravity; but this, when operating upon such small quantities, not only requires fine apparatus, but also much skill, and must consequently often remain

undone. A portion of the fluid may afterwards be poured into a metallic or porcelain capsule, when its ignition by means of a burning match may be attempted. If this does not succeed, the capsule may be heated by a spirit-lamp, when the alcohol contained in the water is the first to evaporate, and may be ignited by a burning match. A portion of the distillate may be set aside; and if a considerable quantity still remains, the following experiment may be made with it. The neck of a small glass funnel is loosely closed by means of a small glass rod; some platinum black is then put into the funnel, moistened with a few drops of distilled water, and the alcoholic fluid is then allowed to flow upon it in a very slow stream by means of a cotton thread, which may act as a siphon. A fluid, with an acid reaction, then drops from the funnel; this is carefully neutralized by a few drops of very dilute solution of potash, and evaporated to perfect dryness on the water-bath. A portion of the residue may be added to some very dilute chloride of iron, to obtain the ordinary reaction of the acetates; another portion may be triturated with a small quantity of arsenious acid, and heated in a small test-tube, when the characteristic strong odour of oxide of kakodyle is produced. These two latter tests however require rather larger quantities of acetic acid before they will succeed; as a general rule, the test with the platinum-black, to which the reaction with chromic acid and the test of combustibility may be added, is quite sufficient.

The platinum-black employed for this purpose is precipitated from a very dilute solution of chloride of platinum by means of zinc; it is washed first with muriatic acid, then with nitric acid, and lastly with potash. The author concludes with a series of experiments, which sufficiently prove the applicability of the method.—Strauch's *Inaugural Dissertation*, Dorpat, 1852.

On the Recognition of Blood-spots upon Linen and Cotton Stuffs. By C. Wiehr.

In the course of last year the author had to examine some pieces of stuffs which bore red spots; these were a dirty old piece of coarse unbleached linen and a blue and white checked pillow-cover. The object was to ascertain whether the red spots upon them were produced by blood.

With this object, a red fragment was cut out of each piece of stuff, and each fragment extracted separately with distilled water. The spots on the coarse cloth had already begun to decompose, as it had lain a long time buried in dung. The filtered fluid from it had a dingy brownish-red colour. By the employment of the reagents, such as liquid chlorine, ammonia, nitric acid and tincture of galls, which are particularly adapted for the detection of albumen, the proper reactions were certainly obtained; but as the fluid was not of a pure red colour, they were not so distinct as to enable the presence of blood to be determined with perfect certainty. With the second fluid from the pillow-cover, which had a dark violet colour, from the bad blue which was produced by logwood, these

reagents could not be employed. The author endeavoured to produce cyanide of potassium with the supposed blood-spots of these stuffs. For this purpose, having first ascertained, in the well-known manner, that the stuff contained no wool, he roasted a red fragment of the coarse linen in a porcelain crucible until it could be rubbed to powder; this powder was mixed with some carbonate of potash, and strongly heated to redness. The calcined mixture was extracted with distilled water, and a little solution of a salt of protoxide, and another of peroxide of iron, mixed with the filtered fluid, by which means a precipitate of indeterminate colour, consisting of protoxide and peroxide of iron, precipitated by the excess of carbonate of potash and protopercyanide of iron, was produced. A little dilute sulphuric acid was now added, by which the oxides of iron were dissolved; whilst, on the other hand, the protopercyanide of iron, which is insoluble in sulphuric acid, made its appearance with its blue colour. The same result was obtained with a piece of the checked stuff on which red spots existed, but not with fragments of the stuffs which presented no appearance of blood-spots.

The experiments were also frequently repeated with other blood, and furnished satisfactory results even with the smallest quantities.

The operation also succeeds when a piece of stuff spotted with blood is boiled with solution of caustic potash, the fluid evaporated to dryness and calcined, and then treated with iron salts and sulphuric acid. This method may also be employed when blood-spots are found upon metallic objects; the spots are dissolved from the metal by solution of potash.—*Archiv der Pharm.*, lxxviii. p. 21.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Method of rapidly bleaching Wax, and purifying Tallow, Oils, &c.

Wax, properly speaking, consists of pure wax and a colouring matter; there are several kinds of wax, distinguished commercially by the relative amount of colouring matter which they contain. Formerly it was supposed that wax could only be bleached by the action of sunlight; to effect this object, the operations could only be commenced in the month of May, when the fine season has set in, and the sun attained sufficient altitude to send its rays more directly, for a longer period and with more force; and these conditions continue only at most for three or four months. To bleach wax by this process, it must be made into ribbons of great tenuity, or feathered as zinc is by being poured into water; an operation which must be repeated at least three times, whilst the duration of the exposure to the sunlight must occupy from one month to six weeks, in order to destroy the colouring matter to which we have alluded. To do this requires a considerable space, which is often very expensive, and a heavy outlay in plant, such as bleaching frames, canvas, &c.; this primitive condition of the wax industry

renders the bleaching not only embarrassing, but uncertain and variable according to the weather.

In order to diminish the amount of capital which was required to be sunk in this branch of trade, and above all to shorten the time required to bleach the wax, M. Cassgrand, some years ago, patented a process in France, which has now passed into the public domain, and which, it appears, has been very successful.

This process consists in melting the wax by means of steam until it becomes very liquid, and then passing it, along with the steam, through a kind of serpentine or worm, by which a large surface becomes exposed to the action of the steam. After traversing the worm, it is received in a pan with a double bottom heated by steam, where water is added in order to wash it; from this it is elevated by a pump, kept hot by steam, into another pan similarly heated, and where it is also treated with water, and is again passed through the serpentine. This operation is repeated twice, thrice, or four times, according to the quality of the wax; during the passage with the steam through the worm, it becomes denser by, it is said, absorbing water (perhaps mechanically?), and deposits in the upper pan. It is allowed to repose in this for about four or five minutes after each passage; and after the last one, about one or two hours, according to quantity, in order to allow of any impurities to subside. The wax is then granulated in the ordinary way by means of cold water, is allowed to dry during two or three days, and the action of light and air does the rest, for which one person is sufficient. The whole of the operations do not require more than a few days, are perfectly certain, and are attended with no danger. Independent of the advantage which such an apparatus has for bleaching wax, it has also that of enabling its qualities, according to relative whiteness, to be distinguished; for this purpose it is only necessary to present the wax in mass to the end of the worm, and in a second or two the vapour determines the relative colour which it will yield.

This process is also applicable to the purification of tallows and of oils; even fish-oil, when passed through the apparatus of M. Cassgrand, and washed as just described, is completely deprived of its disagreeable smell; and if it be set aside in a place where the temperature only reaches from 59° to 68° F., a fresh deposit will form, and the oil will become perfectly clarified and nearly colourless.

This process has considerable analogy with one which Mr. Dixon, of Dublin, patented some time since for bleaching palm-oil, the principle of which was exposing the oil to the action of steam. Cassgrand's apparatus might, no doubt, be applied to the same purpose, and appears to us to have certain advantages over that of Dixon, especially in exposing a larger surface to the action of the steam, and varying that surface oftener. If not already known here, the process is worthy of the serious attention of soap-boilers. Such a method would evidently be much more effective than the present system of purifying oils, especially where sulphuric acid is used, which is almost universally the case. As that acid is scarcely ever effectively removed, many samples of trotter, rape, and other similar

oils, are usually quite acid; where the former is used for the manufacture of hair-oil, it is very destructive to the hair, and the latter destroys the lamps when used for burning, &c. The only modification required for the purification of oil would be to divide the oil as much as possible by means of a diaphragm of copper, pierced with holes, in the first steam-vessel, and thus expose the largest possible surface to the action of the steam in flowing through the pierced diaphragm into the worm.—*Dublin Journal of Industrial Progress.*

On the decolorizing Action of Oxide of Manganese upon Glass. By Prof. Liebig.

It is well known that the addition of small quantities of oxide of manganese is regarded as indispensable in the preparation of white glass; it only exerts a favourable action in those glasses which would otherwise have a green tinge from protoxide of iron.

Nothing certain is known as to the mode of action of the oxide of manganese; it is generally supposed that it serves to convert the protoxide of iron into peroxide, which gives a much fainter pale yellow colour to the glass, so slight indeed that in thin sheets it is scarcely perceptible. It is very rare however to find either crown or sheet glass which is yellow even in thick masses; the glass then usually exhibits a blue or green colour, or is quite colourless.

The oxide of manganese cannot be replaced in the glass mixture by nitrate of potash or other oxidizing substances, the action of which commences as soon as the glass begins to fuse; and I regard it as extremely probable that the manganese of the oxide acts by the colour which as protoxide it communicates to the glass, just as the green coloration is removed by protoxide of iron, whilst it at the same time loses its own proper colour. This action may easily be proved by an experiment which is very well adapted for a lecture.

If to a concentrated solution of protosulphate of manganese (of a red colour) a solution of protochloride or protosulphate of iron (of a green colour) be added, a perfectly colourless mixture is obtained when the proportions are correctly arranged. The green colour of the protosalt of iron and the red of the protosalt of manganese are complementary colours which neutralize each other.

Their action is analogous to that of dilute solutions of cobalt and nickel, which, when mixed in the correct proportions, furnish a fluid which is neither green nor red, but still is not perfectly colourless; it retains a slight tinge of blue. For the same reason a stick of phosphorus which has been coated with metallic copper in a solution of sulphate of copper appears silver-white when viewed through a stratum of fluid of the right thickness. These phænomena are well known; and it would be interesting, in order to obtain complete proof of the decolorizing action of oxide of manganese upon glass containing protoxide of iron, to try whether the fusion of a glass coloured green by the latter, with another coloured red by protoxide of manganese, would produce a colourless glass.—Liebig's *Annalen*, xc. p. 112.

THE CHEMICAL GAZETTE.

No. CCLXXXIV.—August 15, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Æsculine. *By* C. Zwenger.

The author has investigated æsculine, and obtained results which differ in many respects from those of Rochleder and Schwarz*. The æsculine was prepared by Trommsdorff's method from the bark of the horse-chestnut, and was completely purified. Pure æsculine consists of very small, fine acicular crystals. It is inodorous, has a somewhat bitter taste, and a slightly acid reaction; it fuses at about 320° F. with loss of water, forming a colourless transparent mass, which on cooling solidifies into an amorphous mass, with cracks. When water is poured over fused æsculine, this fluid is rapidly absorbed, and the substance is again converted into the common crystalline æsculine. If it be heated beyond its melting-point, it is decomposed, and cools in a crystalline form. When burnt upon platinum foil, it evolves an odour of burnt sugar, and leaves a coal which burns with difficulty. Its dry distillation furnishes æsculine. It is thrown down from its solution by basic acetate of lead in the form of a pale yellow powder. The lead compound is decomposed by washing. When æsculine is added to a mixture of potash and sulphate of copper in solution, it reduces the peroxide of copper into protoxide. It has the formula $C^{76}H^{46}O^{52}$, or rather $C^{76}H^{41}O^{47}+5HO$. Analysis gave:—

Carbon	49·42	49·44	49·49	76	= 5700·0	49·67
Hydrogen	5·11	5·04	5·22	46	575·0	5·01
Oxygen	45·47	45·52	45·29	52	5200·0	45·32

Æsculine loses 5 atoms of water by fusion. The analysis of fused æsculine gave the following results, agreeing with the formula $C^{76}H^{41}O^{47}$:—

Carbon.....	51·98	76	= 5700·0	52·23
Hydrogen.....	4·63	41	512·5	4·69
Oxygen	43·39	47	4700·0	43·08

Æsculetine, $C^{64}H^{22}O^{28}+5HO$.—This body, so called by Rochleder and Schwarz, is, according to Zwenger, most readily obtained when æsculine is dissolved by heat in tolerably concentrated muriatic acid, and the clear solution thus obtained kept boiling for some time, but not too long. The fluid then usually sets, even during the boiling, into a white, or but slightly coloured crystalline jelly, which

* See Chem. Gaz., 1854, No. 270, p. 30.

consists of nearly pure æsculetine. Cold water is then poured to it, in order to separate the æsculetine as far as possible; the crystals obtained are washed with water until free from muriatic acid, when they are dissolved in hot alcohol, and the solution is precipitated with neutral acetate of lead. The yellow gelatinous precipitate of æsculetine and oxide of lead is washed several times with boiling alcohol, and finally with boiling water, and then decomposed by sulphuretted hydrogen.

Æsculetine crystallizes from water in fine shining needles. It dissolves but sparingly in cold water, but more readily in boiling water. It dissolves with ease in hot alcohol, but is nearly insoluble in æther. It has a bitter and somewhat acrid taste, and has no acid reaction. At 212° F. it loses water, and acquires a yellowish colour; the same takes place *in vacuo* over sulphuric acid. It only fuses at a high temperature; the author has heated it to 518° F. without fusing it. When heated in a watch-glass over a spirit-lamp, it fuses into an oleaginous fluid, which has a yellowish or brownish colour from partial decomposition, and solidifies on cooling into an aggregation of shining and somewhat coloured crystals. Before and during the fusion it is partially volatilized. During dry distillation it is for the most part destroyed, and only a very small quantity of undecomposed æsculetine is found in the receiver. The watery solution of æsculetine, prepared cold, is perfectly colourless by transmitted light; a saturated solution, prepared boiling, is on the contrary of a slight yellowish colour. By reflected light these solutions have a faint blue colour, which is heightened by the addition of dilute carbonate of ammonia, but destroyed by free acids. Alkalies and alkaline earths immediately give a yellow colour to solution of æsculetine; it also becomes yellow when dried at 212° F., losing 6·64–6·77 per cent., or 5 equivs. water. Nitrate of silver is quickly reduced by it when hot, but only after standing for a considerable time when cold. A solution of peroxide of copper in potash is reduced by it to protoxide by boiling. Chloride of iron, as also salts of peroxide of iron in general, produce an intense green colour. This reaction is so sensitive, that in the preparation of æsculetine no filtering-paper must be made use of which contains even a trace of peroxide of iron, as otherwise a green solution is produced. Salts of protoxide of iron, free from peroxide, produce no coloration. With acetate of lead a fine yellow precipitate, of constant composition, is obtained. Nitric acid converts æsculetine into oxalic acid. The most concentrated muriatic acid dissolves it without decomposition, and the æsculetine crystallizes from this solution, as from acid solutions in general, in beautiful large needles and laminæ. Concentrated sulphuric acid decomposes it when heated. The analysis of æsculetine, dried at 212° F., gave,—

Carbon	60·65	60·76	64 =	4800	60·95
Hydrogen	3·53	3·44	22	275	3·49
Oxygen	35·82	35·80	28	2800	35·56

which agrees with that of Rochleder and Schwarz.

Æsculetine and Oxide of Lead, $C^{64}H^{15}O^{21}+7PbO$, when freshly precipitated, is of a pale yellow colour, and after drying at 212° F., forms a dark brittle mass, which furnishes a yellow powder. The freshly precipitated compound dissolves in water in very small quantity, giving it a yellowish colour; after long standing, it separates again partially in crystalline flakes. The dried lead salt is insoluble in water. If æsculetine be precipitated from its alcoholic solution by an alcoholic solution of acetate of lead, the precipitate is less gelatinous and paler in colour. Acids which do not precipitate oxide of lead dissolve the compound readily. The solutions are colourless. Analysis of the substance, dried at 212° F.:—

Carbon	28·41	28·36	64 =	4800·0	28·48
Hydrogen	1·18	1·26	15	187·5	1·11
Oxygen	12·75	12·96	21	2100·0	12·48
Oxide of lead ..	57·66	57·42	7	9761·5	57·93

Hence it appears that the æsculetine has lost 7 equivs. of water, which are replaced by 7 equivs. of oxide of lead.

In the decomposition of æsculine by acids, such as sulphuric and muriatic acids, nothing but æsculetine and grape-sugar is formed. Of this sugar Rochleder and Schwarz found the constitution to be $C^{12}H^{13}O^{13}$; Zwenger ascribes this to imperfect drying. Thus we have—

$$C^{64}H^{27}O^{33}+C^{12}H^{14}O^{14}=C^{76}H^{41}O^{47}.$$

Æsculine undergoes the same splitting when heated to a high temperature, when however the grape-sugar is decomposed. At 320° F. it fuses, with loss of water, forming a colourless fluid, which sets into an amorphous mass on cooling. If this fused æsculine be now heated for some time upon a watch-glass beyond its melting-point, the fused mass acquires a yellow or brownish colour, and the residue on cooling solidifies into a perfectly crystalline mass. These crystals are æsculetine, which may easily be obtained in a pure state by solution of the mass in water, precipitation by acetate of lead, and decomposition of the lead salt by sulphuretted hydrogen. The fluid filtered from the compound of æsculetine and oxide of lead contains the usual products of the decomposition of grape-sugar. This decomposition is exceedingly easily effected, for even soon after the fusion of the æsculine, at a heat very little above its melting-point, vapours, arising from æsculetine, are evolved.—Liebig's *Annalen*, xc. p. 63.

On Cynene. By C. Völckel.

When wormseed oil (*Oleum Cynæ*) is repeatedly distilled over anhydrous phosphoric acid, a great part of the oil is resinified, and another part is converted into a thick and but sparingly volatile oil, with which the cynene is mixed. If the thick oil be treated with sulphuric acid, the cynene collects on the surface, whilst the sulphuric acid modifies and dissolves the thick oil, and retains it in solution. When dried over chloride of calcium, this oil begins to

boil at 320° F., its boiling-point rises to 343° F., and between this temperature and 347° F. the cynene goes over. Analyses gave 88·79 carbon and 11·13 hydrogen, agreeing with the formula $C^{12} H^{9}$. Cynene is therefore produced from wormseed oil, $C^{12} H^{10} O$, by the elimination of the elements of 1 equiv. water. It smells like wormseed oil, and burns with a very luminous sooty flame. Its specific gravity at 62°·6 F.=0·825. With fuming sulphuric acid it forms a conjugate sulphuric acid.—Liebig's *Annalen*, lxxxix. p. 358.

On the Decomposition of Brucine by Nitric Acid.
By A. Strecker.

The remarkable reaction of brucine with nitric acid, in which these two colourless bodies, as soon as they come in contact, acquire a red colour with disengagement of some gas, has not yet been explained, notwithstanding the experiments of Gerhardt, Liebig, Laurent and Rosengarten.

Gerhardt found that the gas disengaged in this reaction, which he did not succeed in condensing, possessed the odour and some other properties of nitrous æther ($C^{4} H^{5} O, NO^{3}$), so that he felt no doubt that it was nitrous æther. Liebig, by the reaction of nitric acid (perhaps diluted), obtained a liquid which was heavier than water, and only boiled at 158° F., consequently quite different from nitrous æther. Laurent, repeating Gerhardt's experiments with a cooled receiver, condensed a liquid, which he rectified, without apparent boiling, at a temperature not higher than 50° F.; its analysis gave him 29·0 per cent. of carbon and 6·1 per cent. of hydrogen. Although nitrous æther contains 32·0 per cent. of carbon and 6·6 per cent. of hydrogen, Laurent thinks that he has proved the liquid analysed to have been nitrous æther. He also analysed the yellow body remaining in the retort after the completion of the decomposition of brucine by nitric acid. From two not very concordant analyses of this substance, to which Laurent gives the name of *cacotheline*, he arrives at the formula $C^{42} H^{22} N^{4} O^{20}$, and he represents the decomposition of brucine by the equation—

$$C^{48} H^{26} N^{2} O^{8} + 3NO^{6} H = C^{42} H^{22} N^{4} O^{20} + C^{4} H^{5} O, NO^{2} + 2HO.$$

Brucine. Cacotheline. Nitrous æther.

Rosengarten, who has endeavoured to check this formula by quantitative determinations, found that the inflammable volatile body developed contained carbon and hydrogen nearly in the proportion of 4 : 6 equivs., so that it could not be pure nitrous æther. Moreover, his analysis of the yellow body furnished numbers which, although approaching Laurent's formula, did not agree with it exactly. As he could neither condense the volatile product, nor determine the equivalent of cacotheline by the analysis of its combinations, the only conclusion to which Rosengarten was led by his experiments is, that the decomposition of brucine is not really represented by Laurent's formula.

I felt it to be a question of the highest interest to ascertain whether nitrous æther was formed in this reaction, as this would be

the first example of the formation of æthyle compounds from any substance besides sugar and alcohol. As to æthylamine which has been said to have been obtained from different alkaloids, nothing proves that it was not the isomeric compound, dimethylamine.

I repeated the experiments of Gerhardt and Laurent with 28 grms. of fused brucine; the gas evolved was passed through an apparatus of vessels, of which the first contained a solution of potash of spec. grav. 1·2, the second a solution of protosulphate of iron, and the third of chloride of calcium, whilst the last was surrounded by a freezing mixture of −40° F.

In the cooled receiver a very mobile fluid soon condensed, which quickly changed its original green colour to yellow. Bubbles of gas passed through this liquid throughout the reaction, and acquired a reddish-yellow colour when they came in contact with the air. This condensed liquid (3 to 4 grms.) is extremely volatile; it boils at a temperature of 9°·5 F.; it has an odour like that of nitrous æther, and burns with a pale and slightly greenish flame.

To analyse this liquid, I passed its vapour over oxide of copper and metallic copper heated to redness, and determined the relation between the carbonic acid and water, and in another experiment that between the carbonic acid and nitrogen. In this manner I ascertained the proportions to be $C^2 H^3 N$. Another portion of the liquid was decomposed by an alcoholic solution of potash. After some time crystals of nitrite of potash were deposited, which I converted into nitrite of silver. These experiments prove clearly that this fluid is nitrite of methyle, $C^2 H^3 O, NO^3$.

I also prepared this new compound by means of wood-spirit, nitric acid and arsenious acid, when it exhibited the same properties as the volatile body of brucine, and analysis gave the same composition.

The reaction of nitric acid upon brucine takes place so exactly, that it allows of the determination of the quantity of nitrite of methyle which is developed from 1 equiv. of brucine. For this purpose I made use of an apparatus similar to the former; but instead of condensing the product, I burnt it with oxide of copper, and determined the quantity of carbonic acid and water. In this manner I found that 1 equiv. of brucine (394 parts) furnished 2·1 equivs. of carbonic acid and 2·98 equivs. of water, arising from 1 equiv. of nitrite of methyle.

These results agree with the experiments of Gerhardt and Rosengarten, although these chemists did not discover the true nature of the volatile product; but I cannot understand the results obtained by Laurent. As to the product obtained by Liebig, I take it to be nitrate of methyle, which, according to Dumas and Peligot, boils at 151° F., and is heavier than water. I suppose that the nitrous acid in the hot dilute fluid has become converted into nitric acid and oxide of nitrogen, of which the former has combined with the oxide of methyle.

With regard to the non-volatile products of the reaction, I am equally at variance with Laurent. The yellow compound which is precipitated when the acid liquid of the retort is diluted with water,

and which I call cacotheline, is not the only non-volatile product; a very large quantity of oxalic acid is also formed. Amongst the volatile products, moreover, I found oxide of nitrogen in very large quantity, and some carbonic acid; the latter is however only a secondary product of the oxalic acid. For cacotheline I obtained the formula $C^{40}H^{22}N^4O^{18}$:—

	Found (Average).		Calculated.
Carbon	52·1	40	51·9
Hydrogen	4·9	22	4·8
Nitrogen	12·6	4	12·1
Oxygen	..	18	31·2

I proved this formula in two ways. I determined the quantity of oxalic and carbonic acids formed by the action of nitric acid upon brucine, and found that of the 46 equivs. of carbon of the brucine, 4 equivs. separated in the form of carbonic and oxalic acids. Then by deducting these 4C, and the 2C of the methyle from the 46C of the brucine, we find that cacotheline should contain 40C.

On the other hand, I succeeded in determining the equivalent of cacotheline by the analysis of some definite compounds. In fact, cacotheline is a nitrogen base, but the combinations of this base with acids are decomposed by water. When a solution of chloride of platinum is poured into a solution of cacotheline in muriatic acid, a crystalline precipitate is formed in a few hours, containing 14·8 per cent. of platinum. This agrees with the formula $C^{40}H^{22}N^4O^{18}+HCl+PtHCl^2$.

Cacotheline also combines with metallic oxides; with baryta I prepared a soluble compound of the constitution $C^{40}H^{22}N^4O^{18}+BaO$. According to these experiments the decomposition of brucine by nitric acid is represented by the equation—

$$C^{46}H^{26}N^2O^8+5(HO,NO^5)=\underset{\text{Cacotheline.}}{C^{40}H^{22}N^4O^{18}}+\underset{\text{Nitrite of methyle.}}{C^2H^3O,NO^3}$$
$$+\underset{\text{Oxalic acid.}}{C^4H^2O^8}+2NO^2+4HO.$$

Brucine consequently contains carbon in three different groups—one is methyle; the others are converted by nitric acid into cacotheline and oxalic acid. Cacotheline is doubtless a nitride compound, containing 2 equivs. of hyponitrous acid, so that it is derived from the normal base $C^{40}H^{24}N^2O^{10}$, which only differs from quinine by 6 equivs. of oxygen.—*Comptes Rendus*, July 3, 1854, p. 52.

On the Constituents of the Butter of Cocoa.
By C. Specht *and* A. Gössmann.

This substance has already been repeatedly examined. Boussingault found it to be composed of stearine and oleine; Stenhouse ascertained the presence of stearic acid, considered the existence of margaric acid not improbable, and concluded, from the occurrence of sebacic acid in the product of its distillation, that it also contained oleic acid.

The cocoa-butter examined by the authors, which was obtained from Hoyer's chocolate manufactory in Oldenburg, had a yellowish-white colour and a mild taste; it melted between 85° and 86° F., and solidified at 54° to 56° F. It was saponified with a tolerably concentrated solution of soda; the saponification took place very slowly. The soap obtained was decomposed in the usual manner, the fatty acids freed from adherent salts, and then dissolved in alcohol. This alcoholic solution was submitted to fractional precipitation by a solution of acetate of magnesia in alcohol. In the first precipitations a quantity of acetate of magnesia corresponding with one-tenth to one-twelfth of the fatty acids was employed; the operation was carried on at a temperature of 122° to 140° F., and the magnesia salt collected upon a filter after a few hours.

The acids separated by the two first precipitations melted between 144°·5 and 152°·6 F.; they were then again divided, and the portions which melted at 152°·6 F. recrystallized from alcohol. After the second crystallization they nearly always showed a constant melting-point of 157° F., and the properties of pure stearic acid. Some analyses confirmed this:—

	Found.		Calculated.	
Carbon	75·89	..	36	76·06
Hydrogen	12·81	12·64	36	12·68
Oxygen	..	..	4	11·26

The mother-liquors of the two first precipitates, as well as the solution of the other fatty acids, which could no longer be precipitated by acetate of magnesia from the alcoholic solution in consequence of the presence of free acetic acid, were now freed from this acid, and rendered slightly alkaline by means of concentrated ammonia, and then mixed with an excess of acetate of magnesia. After the mixture had been standing for several days, and the precipitate, which was very small in proportion, no longer increased in quantity, it was filtered. On decomposition it furnished an acid which melted at 129° F., and after recrystallization acquired a constant melting-point of 143°·6 F. Its melting-point, its fine laminar texture, &c., left no doubt that it was palmitic acid. It is contained in the cocoa-butter in such very small quantity, that in operating upon 120 grms. of pure fatty acid, scarcely sufficient material for analysis could be obtained, although scarcely any of it could have been lost by the process adopted.

The ammoniacal alcoholic filtrate was mixed with the mother-liquor of the palmitic acid, nearly neutralized with acetic acid, mixed with acetate of lead, and left for some days. The lead precipitate was extracted with æther; the residue contained, besides carbonate and basic acetate of lead, a small quantity of the lead salt of a fixed fatty acid, probably a residue of palmitic acid.

The ætherial solution was decomposed by very dilute muriatic acid in the cold, concentrated, and left in the cold to crystallize. By the assistance of the low temperature, oleic acid was obtained in groups of dazzling white crystals. The supernatant ætherial fluid

was coloured yellow by altered oleic acid. The altered oleic acid consequently appears to have this in common with its baryta salt, that it crystallizes with more difficulty than the unchanged product. An elementary analysis appeared unnecessary, from the characteristic nature of the physical properties of the acid, as well as its behaviour with baryta.

It appears therefore that cocoa-butter consists of stearine, palmitine and oleine. The stearic acid is present in such a predominating proportion, that this fat must be regarded as one of the best materials for the preparation of pure stearic acid.—*Ann. der Chem. und Pharm.*, xc. p. 126.

On Valeraldine, a Sulphur-base obtained from Valeral-ammonia. By F. Beissenhirtz.

The author has investigated the action of sulphuretted hydrogen upon valeral-ammonia, in the expectation that a base would be formed analogous to the *thialdine* discovered by Wöhler and Liebig*. This expectation was well founded, as the following experiments show:—

Valeral-ammonia was diffused in water; some ammonia was added, and a current of sulphuretted hydrogen passed through the mixture. The crystals gradually disappeared, whilst the basic compound collected on the surface of the fluid in the form of a thick oil. It possesses an unpleasant, but not very strong odour; it is insoluble in water, but soluble in alcohol and æther; it has an alkaline reaction, does not become solid in a mixture of common salt and snow, and is volatilized by heat without apparent decomposition.

Its composition is $C^{30} H^{31} NS^4$, and its formation from valeral-ammonia is analogous to that of thialdine from aldehyde-ammonia:—

$$\underbrace{3(C^4\ H^4\ O^2, NH^3)}_{\text{Aldehyde-ammonia.}} + 6HS = \underbrace{C^{12} H^{13} NS^4}_{\text{Thialdine.}} + 6HO + 2NH^4\ S.$$

$$\underbrace{3(C^{10} H^{10} O^2, NH^3)}_{\text{Valeral-ammonia.}} + 6HS = \underbrace{C^{30} H^{31} NS^4}_{\text{Valeraldine.}} + 6HO + 2NH^4\ S.$$

As this compound is difficult to obtain pure in the isolated form, the author preferred analysing the muriate.

Muriate of Valeraldine.—The oil above mentioned solidifies when muriatic acid is poured over it; the solid mass is soluble in hot alcohol, from which it crystallizes in white needles. From its watery solution nitrate of silver first throws down chloride of silver, which soon becomes black from the separation of sulphuret of silver; by heating it in a closed vessel, all the sulphur contained in it may be separated. For analysis it was dried over sulphuric acid. Analysis:—

* See Chem. Gaz., vol. v. p. 67.

	Found.			Calculated.
Carbon	54·01	30 =	180	55·38
Hydrogen	10·00	32	32	9·84
Nitrogen	4·66	1	14	4·00
Sulphur.....	19·60	4	64	19·69
Chlorine	10·84	1	35·4	10·76

giving the formula $C^{30} H^{31} NS^4, HCl$. The author was prevented by want of material from preparing any other compounds of the base. The valeral-ammonia employed was obtained as a collateral product in the preparation of valerianic acid from fusel-oil by chromate of potash and sulphuric acid. The valerianic acid which passes over is neutralized by carbonate of soda, and the non-acid products removed by distillation; when ammonia is added to these, crystals of valeral-ammonia are immediately formed, and their deposition continues for months. Strecker's statement, that valeral cannot be produced from fusel-oil, consequently requires correction. An attempt to prepare the crystals from the products of the dry distillation of valerianate of baryta did not succeed.

It is probable that there exists a series of compounds isomeric with the true aldehydes, apparently possessing the common property of combining with ammonia, which are formed by the dry distillation of some salts of the acids to which they belong. This opinion has already been expressed by Guckelberger with respect to butyral.

The author failed in preparing butyral-ammonia from butyral, obtained by the distillation of butyrate of lime. It contained butyrone. When the mixed products (butyral, butyrone, &c.) were submitted to fractional distillation, only a few drops, out of several ounces of fluid employed, passed over below 212° F.; the quantity was too small for combustion. Ammonia leaves it unchanged. The boiling-point rose uniformly from 212° F., without becoming stationary at any point, even when the separate portions collected at each interval of 18° F. were again submitted to the same operation. As Chancel states the boiling-point of butyral at 203° F., the author supposed at first that he had a different product under examination. The following analyses however show that, in fact, between 212° F. and 291° F., mixtures of butyrone and the substance isomeric with butyral distil over:—

	Butyral, $C^8 H^8 O^2$.	Boiling-point, 212° F.	Boiling-point, 239°–243° F.	Boiling-point, 275°–284° F.	Butyrone, $C^{14} H^{14} O^2$.
C	66·67	65·73	68·99	72·07	73·69
H	11·11	11·12	11·51	12·07	12·28
O	22·22	..	..	..	14·03

Liebig's *Annalen*, xc. p. 109.

On a new Mode of Formation of Propionic Acid.
By A. Strecker.

If, according to Bensch's process, a mixture of cane-sugar (boiled with a little tartaric acid), chalk, and old cheese be left in a warm

place (86° F.) for eight or ten days, the mass forms a thick paste of lactate of lime. The mother-liquors contain a very small quantity of mannite, which can only be extracted with difficulty. But, from my experiments, the same mixture at a low temperature behaves quite differently; the fermentation then takes place slowly, and the quantity of mannite formed is very large. When this, prepared according to Bensch's directions with 5 kilogrms. of sugar, was left in winter in a room which was only heated during the day, crusts of lactate of lime were only formed at the end of two or three months; the mother-liquor, concentrated by evaporation, furnished more lactate of lime, but also a multitude of crystals of mannite, which were easily purified by repeated crystallization. It appeared to me that the quantity of lactate of lime formed did not exceed that of the mannite. The experiments of Pelouze and Gay-Lussac have shown that the juice of the beet-root also furnishes a great deal of mannite during the viscous fermentation; but this fermentation takes place under different circumstances.

A mixture which had deposited crusts of lactate of lime was left during summer in a place of which the temperature did not exceed 58°–62° F., the water lost by evaporation being renewed from time to time. After some months the volatile acids formed were isolated. There was no trace of butyric acid, but large quantities of propionic and acetic acids. I separated the two acids by Liebig's method—partial saturation with potash and distillation. The propionic acid passes first, and the residue contains the acetic acid.

With this propionic acid I prepared the following salts, which were analysed:—

$KO, C^6 H^5 O^3$, in delicate lamellæ.

$NaO, C^6 H^5 O^3 + 2HO$, an amorphous mass, dried in the air.

$BaO, C^6 H^5 O^3 + HO$, in crystals of the rhombic system, soluble in 1·3 part of water at 59° F.

$CaO, C^6 H^5 O^3 + HO$, in silky laminæ.

$CaO, C^6 H^5 O^3 + HO$, in green crystals, probably isomorphous with the acetate.

$2PbO, C^6 H^5 O^3$, in acicular crystals.—*Comptes Rendus*, July 3, 1854, p. 56.

On a new Method for the Preparation of Benzoglycolic Acid.

By A. Gössmann.

Strecker regards hippuric acid as the amidogen acid of the non-nitrogenous benzoglycolic acid, $C^{18} H^8 O^8 = HO + C^{18} H^7 O^7$. Socoloff and Strecker, who first particularly investigated benzoglycolic acid*, found it to be a conjugate acid, which was very easily resolved into benzoic and glycolic acids by the action of concentrated acids and bases, and even when boiled by itself in water, by taking up 2 atoms of water. They employed Piria's process for the decomposition of the amidogen acids with nitrous acid. Direct introduction

* Chem. Gaz., vol. x. p. 81.

of nitrous acid into the watery solution of hippuric acid furnished less favourable results than the passage of nitrous acid into a pasty mixture of hippuric acid and nitric acid; the disadvantages of this plan, which occurred to both authors, are, that no direct indication of the completion of the operation could be given, and besides that the unavoidable heating of the mixture with the concentrated nitric acid always effected a partial decomposition of the benzoglycolic acid.

I therefore adopted the following method of decomposing hippuric acid, which, as far as I know, is quite new. I dissolved hippuric acid in an excess of rather dilute solution of potash, and passed a slow current of chlorine gas into the cold solution, with the view of employing the oxygen displaced by the chlorine in the decomposition of the amide, instead of in the formation of hypochlorite of potash. My expectation was confirmed; a violent evolution of nitrogen gas took place. As soon as this was terminated, the passage of the chlorine was interrupted, the hypochloric acid was expelled, and the excess of alkali carefully neutralized by muriatic acid; the fluid was then concentrated by a gentle heat, and rendered distinctly acid by dilute muriatic acid. If the concentration has been correctly performed, the entire solution sets into a crystalline jelly of benzoglycolic acid; if it be then kept warm for a short time, this acid separates from the supersaturated solution in yellow oleaginous drops, which on cooling solidify into a crystalline mass; this, perhaps, is a characteristic property. By gentle evaporation after neutralization of the free muriatic acid, a further quantity of acid may be obtained.

Its purification may be effected either according to Strecker's directions from the lime salt, or in the following manner:—The acid is dissolved in æther, and the ætherial solution poured into a retort over a proportionably small stratum of water; the æther is then carefully distilled off, and in proportion as this disappears the water takes up the acid; when this is saturated, the excess of acid separates in the oleaginous form, but quite free from any undecomposed hippuric or benzoic acids.

The physical properties of the acid agree exactly with those given by Strecker. Besides the properties already referred to, it is characterized by its fine acicular crystallization, its ready solubility in æther, the properties of its silver salt, by the results of its analysis for carbon and hydrogen, and lastly, by the absence of nitrogen. The presence of the latter is the best proof of the existence of hippuric acid, for the determination of the carbon and hydrogen can scarcely lead to definite conclusions, as the two acids nearly agree in these respects. The presence of benzoic acid is, of course, readily detected by the higher amount of carbon, benzoic acid containing about 8 per cent. more carbon than either of the other acids.

If we consider the theory of the process and the peculiarities of benzoglycolic acid, the rules for the conduct of the operation must follow of themselves, *i. e.* an excess of alkali must always be present during the passage of the chlorine; the mixture must be kept as cool as possible during the operation, and lastly, during the concen-

tration the presence of an excess of mineral acid must be avoided as much as possible. If an excess of chlorine be set in action, a yellow oleaginous body separates within twenty-four hours, and often still earlier; this is apparently continually undergoing decomposition, and is probably a chlorinated product of benzoic acid. The entire operation is easily performed, and the direct action of the chlorine is so easily prevented, that this process appears to me to be applicable to the decomposition of other amidogen acids.—Liebig's *Annalen*, xc. p. 181.

ANALYTICAL CHEMISTRY.

On the Determination of Alumina and Oxide of Iron. *By* F. von Kobell.

It is well known how slowly the complete washing of the hydrate of alumina obtained in the usual method of separating this earth from oxide of iron is effected; and, in fact, the amount of alumina is often stated too high in analyses, in consequence of its not having been sufficiently washed. The author consequently proposes the following method for abridging the process, and leading, he thinks, to a more exact determination of the earth.

The hydrate of alumina is precipitated in the usual way and filtered. When water has been once poured over it, he allows the precipitate to dry, and then heats it with the filter in a platinum crucible until the commencement of a red heat. The brittle mass is now triturated with water and filtered again. The washing is then rapidly effected, and the earth, after being well calcined, is weighed. (This product, when dissolved in sulphuric acid and precipitated with ammonia, still had exactly the same weight.) The wash-water from the last washing, when evaporated, furnished a considerable quantity of chloride of potassium, which however was perfectly free from alumina.

The washing of hydrated alumina is rendered difficult by the gelatinous consistency of the precipitate; by drying and heating as above described, the greater part of the water is got rid of, and the pounded earth may be washed as readily as sand. The incipient red heat necessary for this purpose is insufficient for the decomposition of the chloride of potassium.

The usual method of determining the oxide of iron separated from the alumina is to dissolve it in muriatic acid, precipitate it by ammonia, and then only to determine its quantity; but in this way a loss very readily takes place. The oxide of iron thus obtained may however be determined without dissolving it again in muriatic acid, by heating it to redness with the filter, and then triturating it with water, when it may easily be freed from any small quantity of potash by washing with water. A quantity obtained in this manner, when dissolved in muriatic acid and precipitated by ammonia, did not exhibit the least difference in weight.—Liebig's *Annalen*, xc. p. 251.

Preliminary Note on the Determination of Oxygen in non-azotized Organic Bodies. By E. H. von Baumhauer.

The author, after referring to the errors which necessarily arise from the present mode of calculating the amount of oxygen in organic bodies, and stating that he has long been occupied in the endeavour to find some process for the direct determination of this element, gives the following description of a process for ascertaining the amount of oxygen contained in non-azotized organic bodies:—

"The principle upon which my process is founded is as follows:—All organic compounds contain a smaller amount of oxygen than is necessary for the oxidation of the carbon into carbonic acid, and of the hydrogen into water. During ignition with oxide of copper, the latter furnishes oxygen for the formation of carbonic acid and water. If the oxygen extracted from the oxide of copper be deducted from that contained in the carbonic acid and water, the remainder gives the amount of oxygen in the substance. The oxygen given off by the oxide of copper is determined in the following manner:—The substance under examination is, as usual, mixed and heated with oxide of copper in a glass tube open at both ends. The carbonic acid and water are also collected in the usual manner. The two ends of the apparatus are connected with exactly-graduated glass tubes, of which the one behind the combustion-tube is filled with oxygen gas. After the completion of the combustion, this oxygen is passed over the red-hot oxide and reduced copper. When the apparatus is perfectly cool, the amount of gas in the two divided tubes is read off, which must also be done before the commencement of the experiment; the weight of the carbonic acid and water is then determined. After making the corrections for the state of the barometer and thermometer, the volume of gas contained in the two tubes after the combustion is deducted from their contents before the experiment; the difference is the quantity of oxygen which was taken up by the reduced oxide of copper.

"The following may serve as examples of the exactitude of this method:—0·9895 grm. of oxalic acid gave 0·969 of carbonic acid and 0·203 water. The corrected volume of the gas in the whole apparatus before the combustion was 485·90 cub. centims.; after that operation, 360·33 cub. centims. If we calculate the per-centage composition of oxalic acid from these data, we get—

	Found.		Calculated.
Carbon	26·71	12	26·66
Hydrogen	2·28	1	2·23
Oxygen	71·32	32	71·11

"0·9585 grm. of oxalate of lead gave 0·2865 carbonic acid; the corrected volume of gas before combustion was 462·29, afterwards 426·29 cub. centims.; hence—

	Found.	Calculated.
Carbon	8·15	8·13
Oxygen	16·30	16·26

"With nitrogenous substances I hope to determine the amount of carbon, hydrogen, oxygen, and nitrogen in the same manner, at one operation, and with the same portion of substance, with this difference, that before combustion the entire apparatus will have to be filled with oxygen, and that at the conclusion all the nitrogen set free will be driven by oxygen into the graduated tube, in which it may be determined after the absorption of the oxygen by pyrogallate of potash."—Liebig's *Annalen*, xc. p. 228.

New Test for Sugar. By J. Horsley.

If a freely alkaline solution of chromate of potash be mixed with urine containing sugar, and boiled, the liquid will assume a deep sap-green colour, arising from the decomposition of the chromic acid, the reduced oxide of chromium being held in suspension by the potash. Such is the sensitiveness of this test, that 5 or 6 drops of saccharine urine diffused through water is sufficient to show the effect, which is infinitely more striking than even Moore's potash, or Trommer's copper-test.—*Med. Times and Gazette*, July 15, 1854.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 15, 1854. (The Earl of Rosse, President, in the Chair.)

"Examination of the Cerebro-spinal Fluid." By William Turner, Esq., Scholar of St. Bartholomew's Hospital.

In the Bulletin de l'Académie de Médecine for December 1852, a paper is published by M. Bussy, containing an analysis by M. Deschamps of a fluid, which flowed from the ear of a man who had sustained a fracture of the base of the cranium. From a comparison between the composition of this fluid and that given by M. Lassaigne as the composition of the cerebro-spinal fluid, M. Bussy arrived at the conclusion that they were identical in their origin. In addition, however, to the albumen and ordinary saline constituents, M. Deschamps found that the fluid obtained from the fractured cranium contained a certain constituent which possessed the peculiar property of reducing the blue protoxide of copper to the state of the yellow suboxide.

As this power of reducing the oxide of copper is possessed also by grape-sugar, M. Bussy arrived at the conclusion that this fluid contained a small portion of grape-sugar, and as additional evidence in support of this conclusion he quotes the experiments of M. Bernard, who, by irritating the base of the encephalon and the origin of the vagus nerve, produced an excess of sugar in the secretions. He supposes that in the present instance the fracture through the base of the cranium may have produced some irritation at the origin of the pneumogastric, and thus have excited the formation of sugar.

Such a supposition would have received additional confirmation if at the same time an analysis could have been made of the blood, urine, or other secretions, so as to determine if sugar was present in those fluids—no such analysis however is given. The property of reducing the oxide of copper was also found by M. Bussy to reside in the cerebro-spinal fluid of the Horse and Dog. In none of these experiments was he able to induce fermentation. As this reducing power is not peculiar to grape-sugar, but is possessed by other organic substances, such as lactine and lactucine, this test alone should not be relied on as affording any positive indications of its presence; recourse should therefore be had to other confirmatory experiments.

With a view to determine this point, Mr. Paget, in the early part of March last, gave me for examination three separate portions of the cerebro-spinal fluid, obtained by puncturing a spina bifida in a child, several days intervening between the removal of each portion.

Those removed on the first two occasions were perfectly clear and pellucid, giving an alkaline reaction to test-paper, their spec. grav. being 1·006, no spontaneous coagulation taking place after standing for some time; that removed on the third occasion had a slightly yellow tinge, and a distinct coagulum formed in it on standing. The presence of fibrine in this instance was owing doubtless to some slight inflammation having been set up, caused by the successive puncturings. The three specimens corresponded in the following characters:—

1st. No precipitate on applying heat, merely an opalescence being produced; on the addition of a few drops of nitric acid a white flaky precipitate subsided. Nitric acid alone, without heat, also caused a precipitate.

The non-precipitation of the albumen, until the addition of the acid, was owing to the alkalinity of the fluid.

2nd. Boiled with liquor potassæ a very faint pinkish tint was produced; a few white flakes also fell down.

3rd. Heated in a water-bath with the blue oxide of copper, in a few minutes the yellowish red powdery suboxide precipitated.

This reaction took place both in the original albuminous liquid and after the coagulation of the albumen by heat and nitric acid.

4th. A piece of flannel, saturated with the chloride of tin, was well moistened with the fluid, and then heated over a red-hot coal; no brown colour of the flannel was produced, such as occurs when grape-sugar is present. (Maumenè's test.)

5th. A portion mixed in a test-tube with some German yeast was placed for several hours in a warm cupboard, but there was no development of gas.

From these experiments it appears that of the various tests employed, only one gave any indication of the presence of grape-sugar, that test also being the one which is most liable to deception. The lowness of the specific gravity, in which respect this fluid and that analysed by M. Deschamps closely corresponded, would, *à priori*, almost lead to the assumption that no grape-sugar was present.

The presence of the reducing agent could not in this case depend upon any irritation of the origin of the vagus, for the irritation, if any, produced by a spina bifida is at the end of the cerebro-spinal axis furthest removed from the origin of that nerve. That the material however which effects this reduction is of a very changeable nature, was shown by allowing a portion of the fluid to stand for several days until putrefaction had commenced. The fluid was then filtered so as to separate the insoluble albuminous flakes, and the clear liquid heated in a water-bath with the blue oxide of copper; when, instead of the suboxide being produced, the black anhydrous oxide was formed, just as is the case when the blue oxide is heated merely with water, thus satisfactorily showing that the reducing substance had been destroyed.

The recent investigations of Virchow* and Busk† have shown that substances of a non-nitrogenous nature exist both in the brain and spinal cord, but they hold somewhat different opinions respecting their exact characters; for whilst the former considers them to be cellulose, the latter regards them both in their "structural, chemical and optical properties" to resemble starch. In conformity with these views, it was interesting to determine if any indications of the presence of either of these substances could be found in the cerebro-spinal fluid; accordingly a portion of the fluid was evaporated nearly to dryness and then divided into two portions; to one was added an alcoholic solution of iodine and concentrated sulphuric acid, when a violet tint was produced, which after a few minutes disappeared; but it was also found that this same appearance was produced when the acid and iodine solution were mixed together alone, the violet colour being evidently owing to the volatilization of a part of the iodine and the evolution of its characteristic violet tint; to the other a solution of iodide of potassium and then nitric acid was added, when a brown colour was produced, owing to the liberation of the iodine. In neither portion could it be said that any evidence of the presence of starch or cellulose was detected.

A comparative trial was also made between the effects produced upon the blue oxide of copper by the cerebro-spinal fluid, solutions of grape-sugar, cane-sugar, starch, cellulose, and mannite, an unfermentizable sugar. These various substances were heated in a water-bath for the same length of time, when it was found that whilst the grape-sugar effected a reduction immediately, and the cerebro-spinal fluid only after the lapse of several minutes, neither the starch, cellulose, cane-sugar nor mannite effected any reduction at all.

The power of reducing the blue oxide of copper is not confined to non-nitrogenous substances, for I found that if a solution of leucine† be heated along with it in the usual manner, the reduction is effected in about the same length of time, and in the same way as by the

* Quarterly Journal of Microscopical Science, January 1854. † Ibid.

† Leucine $C^{12}NH^{13}O^4$, a weak base, belonging to the same series as glycocine and alanine, is generally obtained by the decomposition of albuminous substances. It has been obtained by Scherer from the spleen, and, according to Gregory, has been detected as a natural product in the liver of the Calf.

cerebro-spinal fluid. This single experiment is not of itself sufficient evidence that the reducing power in both cases depends upon the presence of the same substance. Such an assertion could only of course be proved by obtaining from the cerebro-spinal fluid leucine in the crystallized form. A proper quantity of the fluid was not, however, left to investigate this point.

From the above experiments I think it may be safely asserted that the power possessed by the cerebro-spinal fluid of reducing the oxide of copper, is not owing to the presence either of grape-sugar or any of the allied substances: whether it may depend upon the presence of leucine or other modifications of albumen of a somewhat similar nature, or whether it may be due to the presence of a substance belonging to another series, is a point that has yet to be determined.

"On the Oxidation of Ammonia in the Human Body." By H. Bence Jones, M.D., F.R.S.

In the last edition of Professor Lehmann's Animal Chemistry, vol. ii. p. 363, a very decided opinion is expressed against the conclusion to which I arrived in consequence of some experiments published in the Philosophical Transactions for 1851.

I considered it proved that ammonia was partly at least converted into nitrous acid in its passage through the body. In opposition to this Professor Lehmann states,—

1st. That the method which I employed must of necessity give a reaction resembling that given by nitrous acid; his words are, "Es wäre nun leicht einzusehen dass schweflige Säure, durch welche bekanntlich Iodwasserstoff zersetzt wird, in die Vorlage übergeht und so jene vermeintliche salpetersaure Reaction bedingt."

2ndly. That when nitric acid was added to urine and it was distilled with phosphoric acid instead of sulphuric acid, no trace of blue colour with starch and iodide of potassium could be obtained. "Das nach Anwendung von Phosphorsäure erhaltene Destillat giebt aber auch jene vermeintliche salpetersaure Reaction nicht, ja selbst dann nicht, wenn dem Harn vorher absichtlich einige Tropfen Salpetersäure zugesetzt worden waren."

It appeared to me undesirable merely to reply to Professor Lehmann, that I had expressly stated that the indigo and protosulphate of iron tests were used, and gave as decided proof of the presence of nitrous acid in the urine as Price's test gave; and that sulphurous acid could not have produced the same effect as nitrous acid in these tests. It seemed more desirable to repeat the experiments which had been made in Professor Lehmann's laboratory on the action of sulphurous acid, and on the effect of using phosphoric instead of sulphuric acid in the distillation of the urine.

I was fortunate enough to obtain the assistance of Mr. Malone to carry on the experiments continuously from day to day, and through the kindness of Dr. Hofmann this was done in the College of Chemistry.

1st. On the action of sulphurous acid on starch and iodide of potassium and very dilute hydrochloric acid.

In England it is by no means well known that sulphurous acid decomposes hydriodic acid. On the contrary, theoretically it should not liberate iodine, and experimentally not only does it not liberate iodine, but it hinders the liberation of iodine and stops the formation of the blue colour when Price's test is used and nitrous acid is present; and if sulphurous acid be added after the blue colour is formed it makes it disappear.

Pure sulphurous acid was prepared, some nitre was fused, and a dilute solution was made, and it was tested by Price's test (starch, iodide of potassium and very dilute hydrochloric acid), then the dilute nitre solution immediately gave the deep blue iodide of starch; but when much or little sulphurous acid was added previously to the nitre solution, no blue colour at all was produced; and when, instead of the nitre solution, much or little sulphurous acid alone was added, contrary to the statement of Lehmann, no decomposition of the hydriodic acid could be obtained.

If instead of pure iodide of potassium it was mixed with iodate of potassa, an immediate blue colour was of course observed. I can only suppose that in this way Professor Lehmann obtained the reaction which he has attributed wrongly to the action of sulphurous acid on hydriodic acid, unless indeed no sulphurous acid at all was present and the acidity of the distillate was unneutralized. Dr. Lehmann is however right as well as wrong, in saying that Price's test for nitric acid fails when sulphurous acid is present. The test fails, not, as he says, because sulphurous acid has the same action as nitrous acid in liberating iodine, but because it has exactly the opposite property of hindering the iodide from being set free even when nitrous acid in small quantity is present.

It is possible that in distilling the urine with sulphuric acid, the distillation, if carried too far, may give rise to sulphurous acid, and that thus Price's test may fail to detect nitrous acid in the urine. Moreover, portions of the distillate may be projected against the sides of the hot retort, by which the sulphuric acid acting on the organic matter may be decomposed, and minute quantities of sulphurous acid may be liberated. This sulphurous acid, instead of decomposing hydriodic acid, causes the reformation of hydriodic acid when nitrous acid liberates iodine in Price's test.

2ndly. Lehmann states that experiments were made by distilling urine to which a few drops of nitric acid were added with phosphoric acid, and that then the distillate gave no reaction with Price's test.

The following experiments were made with every precaution.

Anhydrous phosphoric acid was prepared, and it was found to be free from nitrous acid. Some healthy urine was taken and some pure nitrate of potassa, in the proportion of two grains of salt to an ounce of fluid, and distilled with phosphoric acid (ten ounces of urine, twenty grains of nitre, and one ounce of anhydrous phosphoric acid). On concentrating, the neutralized dilute nitrous acid was detected by all the tests, namely, the indigo test, the protosulphate of iron and Price's test.

In a second experiment, five ounces of urine with five grains of

nitre and half an ounce of anhydrous phosphoric acid, gave nitrous acid by all the tests. The distillation was continued until the contents of the retort were viscid.

In a third experiment, three ounces of urine with a grain and a half of nitre were distilled with three drachms of glacial phosphoric acid; the distillate neutralized and evaporated gave no trace of nitrous acid; the same urine with the same quantity of nitre and three drachms of sulphuric acid, when distilled, gave a distillate, which when neutralized and evaporated gave decided evidence of nitrous acid.

In my former paper I showed that by distilling with sulphuric acid when only one-tenth of a grain of nitre was added to each ounce of urine, nitrous acid could be detected.

From these experiments it appears that distillation with sulphuric acid is to be preferred to distillation with phosphoric acid; but even with this last acid, when a grain of nitre is added to an ounce of urine, the nitrous acid can be detected.

I then endeavoured, by using phosphoric instead of sulphuric acid in distilling urine passed after a salt of ammonia had been taken into the stomach, to detect nitrous acid in the urine.

Two drachms of muriate of ammonia were taken in seven ounces of distilled water. The urine was collected for six hours afterwards. Twelve ounces of this urine were distilled with one ounce of phosphoric acid (anhydrous). The distillate, when concentrated, did not give any evidence of nitrous acid by Price's test.

The same experiment was repeated with no better result.

In another experiment, sulphuric acid, six drachms to twelve ounces of urine, was used instead of phosphoric acid. The distillate as soon as it was obtained gave the slightest precipitate with chloride of barium insoluble in nitric acid, showing that a trace of sulphuric acid was carried over into the receiver. The distillate was made alkaline with pure carbonate of soda, evaporated, and nitrous acid was immediately detected by the indigo and iron test, as well as by Price's test. A portion of the distillate left exposed to the air, on the following day had lost the power of liberating iodine. This arose from the nitrous acid passing into nitric acid.

Pure nitre gives no colour with starch, iodide of potassium and dilute hydrochloric acid, but when fused it produces the liberation of iodine immediately. If the solution of fused nitre is exposed to the air it loses this property, but regains it when the solution is evaporated to dryness and refused and again dissolved.

In another experiment six ounces of urine passed before the muriate of ammonia was taken were distilled with half an ounce of sulphuric acid, the distillate was highly acid, and gave a slight precipitate with chloride of barium; it was made slightly alkaline, evaporated to a small residue, and then gave no evidence of nitrous acid. Then two drachms of muriate of ammonia were taken in seven ounces of distilled water, eight ounces of urine passed four hours afterwards were distilled with half an ounce of sulphuric acid. The distillate was fractional; the first portion gave no colour with starch

test; it contained a minute trace of sulphurous acid. The second portion was highly acid; it was made slightly alkaline, evaporated nearly to dryness, and then gave most positive evidence of nitrous acid by Price's test, and also by decolorizing a deep solution of indigo.

Thus before the salt of ammonia was taken no nitrous acid could be detected in the urine, whilst after the ammonia nitrous acid was proved to be present, not only by Price's test, but by the indigo test also.

In conclusion, it results from these experiments,—1st, That in Price's test sulphurous acid produces exactly the opposite effect to nitrous acid, and even hinders nitrous acid from liberating iodine from hydriodic acid.

2ndly. That phosphoric acid, when mixed with urine containing nitre and distilled very low, does liberate nitrous acid; though when used instead of sulphuric acid, it does not enable the nitrous acid to be detected so readily as when the latter acid is employed.

Hence the experiments performed in Professor Lehmann's laboratory by Herr Jaffé*, do not invalidate Price's test for nitrous acid in the way Professor Lehmann supposes; and by again repeating some of my former experiments, I still arrive at the conclusion that when ammonia is taken into the body nitric acid may be detected in the urine, but that the quantity which can be made to appear is so small that the most delicate method is required for its detection. This however is no proof that a much larger quantity may not be lost in the process for obtaining it from the urine.

"On the frequent Occurrence of Indigo in Human Urine." By Arthur Hill Hassall, M.D.

From the present communication it appears that the occurrence of indigo in human urine is more common than the author was led to anticipate from his first inquiries†.

The author furnishes additional proofs of the blue colouring matter in question being really indigo, by converting it into isatine and aniline.

Contrasting its chemical and physiological relations with hæmatine and urine pigment, he shows that indigo is closely allied in its nature and origin to those substances, and he considers that when indigo is met with in urine in considerable amount, it forms a vehicle for the elimination of any excess of carbon contained in the system. This view is borne out by the important fact, that the greater number of cases in which indigo has been observed to be developed in the urine in large amount have been cases of extensive tubercular disease of the lungs, and in which the decarbonizing functions of those organs are greatly impaired.

* Chem. Gaz., vol. xii. p. 53. † *Ib.*, vol. xi. p. 355.

THE CHEMICAL GAZETTE.

No. CCLXXXV.—September 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of the Halogen Compounds of Æthyle and Amyle on some Vegetable Alkaloids. *By* Mr. Henry How, Assistant to Professor Anderson, Glasgow University.

The memoir which I have now the honour of presenting to the Society contains part of a continued investigation, of which the first results were published in a paper read last year before the Chemical Society of London*. The nature of the materials experimented on is such, and the scope of the subject so large, as to afford nothing more to all I have at present brought to light than the name of a bare and partial outline; yet the facts I have now to adduce, of some interest in themselves, will increase that of those already made known, and prove of additional service in aiding to complete that desirable object, a knowledge of the chemical constitution of the natural bases. In the paper alluded to, I showed that, by the action of iodide of æthyle and of methyle upon morphine and codeine, the two most prominent alkaloids of opium, new salts are produced, in which the basic molecules appear to assimilate by their chemical characters to the hypothetical metal ammonium, or its oxide rather; so that, in the system of Hofmann, these peculiar results of natural, and as yet inimitable agencies, would take rank among the nitryle bases. I say as yet inimitable, because it appeared that although one of the new salts possessed precisely the same centesimal composition as the corresponding salt of codeine, the base contained in the artificial product was widely different in appearance and properties from this alkaloid; a fact which seems to militate against a hope of forming the natural bases by this or similar means, and to show that the building up of these bodies is a process peculiarly the function of the *vis vitæ* of the plants producing them; at least that, easy as the transition of morphine into codeine appears to be on a comparison of their respective rational formulæ, and since the adding the required 2 equivs. of carbon and hydrogen to the former proves of ready performance, the cause of the failure lies deeper than in this difference merely, and that there are peculiarities in the construction of the primary molecules which we are at present as far as ever from being able to imitate. I further remarked, that so far as the amount of basic hydrogen, or compounds supplying its

* Quart. Journ. Chem. Soc., vol. vi.

place, is concerned, the fact that it proved the same in these two alkaloids was possibly to be anticipated from their similar origin; and that I intended pursuing the subject with a view of ascertaining if all the bases of the same plant were so far analogous. It will be seen that they do not appear to be so in reality, my attempts at forming corresponding compounds with some other alkaline principles of opium having been as yet unsuccessful. Another order of plants, however, has furnished me a base, strychnine, which seems in this respect similarly constituted with morphine and codeine, inasmuch as, under the same circumstances, it yielded a new combination, whose stability in the free state, and in some of its salts, caused it to afford more decided results than I was able to obtain with the analogous products from these alkaloids.

In describing the individual reactions, salts, &c., I have preferred giving them, as nearly as is consistent with clearness, in the order in which they were investigated.

Behaviour of Papaverine with Iodide of Æthyle.

Hydriodate of Papaverine.—Next to morphine and codeine, papaverine is the opium alkaloid possessing the most marked characters and highly basic properties; and as I was acquainted with the beautiful substitution products it yielded to Prof. Anderson, of which an account has been given to this Society*, I chose it as the subject for further experiment. Accordingly, some of the base, in small crystals, was placed in a tube, spirit of wine poured on it, and iodide of æthyle added; a great part of the crystals was seen to disappear immediately, and when the sealed tube was placed in boiling water, solution became rapidly complete. The clear fluid was allowed to boil about half an hour, but no solid made its appearance, either during the continuance of the heat, or upon the subsequent cooling and standing of the vessel. The solution was distilled finally in a flask to a very small bulk, and the syrup which remained soon solidified into a crystalline mass; this was found to be perfectly soluble in hot water (papaverine itself being insoluble) and in spirit of wine; but, from peculiarities to be mentioned presently, absolute alcohol was preferred as a solvent. From a concentrated hot solution in this menstruum, the new product was obtained on cooling in rhombic crystals, a portion of which, as they proved to be a hydriodate, was submitted to analysis in the ordinary way, when it gave a per-centage of iodine of 27·02; the theoretical calculation corresponding to the anhydrous hydriodate of papaverine, whose formula is $C^{40}H^{21}NO^{8}HI$, is 27·21.

I shall show presently, from an analysis and description of the base obtained from this salt, that there can be no doubt of its real nature; so that, under these circumstances, papaverine behaves in a manner similar to that shown before† to be the case when hydrated morphine is placed in contact with chloride of amyle, it forms a salt, namely, with the halogen of the æther compound, while no doubt

* Trans. Roy. Soc. Edin., vol. xxi. part 1. † Quart. Journ. Chem. Soc. vol. vi.

the corresponding alcohol is simultaneously generated by the agency of the elements of water, as in the equation—

$$C^{40}H^{21}NO^{8}+C^{4}H^{5}I+2HO=C^{40}H^{21}NO^{8}HI+C^{4}H^{6}O^{2};$$

this, at least, seems the most obvious explanation of the change when water is present. To determine if the formation of the salt were really due to the agency of water, I repeated the experiment with absolute alcohol in place of rectified spirit, and the papaverine was dried at 212°, to remove accidental moisture, its crystals containing no water of combination. In this case, also, the hydriodate was formed from part of the alkaloid, the rest remaining unaltered. The iodide of æthyle had been distilled from chloride of calcium, and I should think could furnish at the most but a minute quantity of water; and it is not easy to see how the reaction is brought about under these circumstances, unless it be assumed that it occurs with the formation of æther. The detection of this substance would not be readily effected upon the small scale upon which I worked, and I therefore only throw out the following equation as a possible explanation of the reaction:—

$$C^{40}H^{21}NO^{8}+C^{4}H^{5}I+C^{4}H^{6}O^{2}=C^{40}H^{21}NO^{8}HI+2C^{4}H^{5}O.$$

As no account has yet been given of the hydriodate of papaverine, a short description of it may be subjoined. The salt is extremely soluble in boiling water, and the moment the heat is withdrawn from a strong solution, the fluid assumes a milky appearance, and an oil is soon deposited, which after some hours passes into the form of stellate colourless needles; it is also soluble in spirits of wine, but in absolute alcohol it dissolves with far less facility, and it requires protracted boiling, when the salt has once taken on the crystalline condition, to obtain perfect solution with this menstruum. The hot liquid deposits the salt rapidly, as it cools, in colourless rhombic crystals. When exposed to a temperature of 212° F., in a dry state, the hydriodate of papaverine assumes a brown tint, loses slightly in weight, and is found to have undergone some decomposition, as it no longer dissolves completely in hot water, but leaves a brown resinous matter.

By addition of ammonia to the mother-liquors of the salt which had been analysed, a white crystalline precipitate was obtained; this was recrystallized from dilute spirit, and burnt with chromate of lead when it yielded:—

Carbon.....	70·63	40	= 240	70·79
Hydrogen.....	6·55	21	21	6·20
Nitrogen	..	1	14	4·10
Oxygen.....	..	8	64	18·91

A glance at the result, and the appended calculation of the numbers required by the formula of papaverine, leaves no doubt as to the base of the salt. I was perfectly satisfied as to its nature, from its appearance and some peculiar well-marked reactions characteristic of papaverine; thus with strong sulphuric acid it yielded a splendid purple fluid at the instant of solution, and when heated with a little

nitric acid became converted into a mass of yellow crystals, which are nitrate of nitropapaverine, described by Dr. Anderson*.

Behaviour of Narcotine with Iodide of Æthyle.

Hydriodate of Narcotine.—The next alkaloid of opium submitted to examination was narcotine; and the following experiment shows its deportment to be perfectly similar to that of papaverine.

Some narcotine in fine powder was heated in a sealed tube with absolute alcohol and iodide of æthyle; after about ten minutes' exposure to a temperature of 212°, the whole of the base disappeared; but to ensure complete decomposition, the heat was continued some twenty minutes longer. When the tube had cooled, and stood a short time, groups of four-sided colourless prisms appeared. On opening the vessel, and submitting these to examination, they proved to be unchanged narcotine, while their mother-liquor was found to contain an hydriodate. The excess of iodide of æthyle and alcohol was accordingly distilled off, and the remaining syrup tested as to its nature; it was almost entirely soluble in boiling water, leaving only a little narcotine, and the solution contained the hydriodate of that base.

This salt is deposited, from a concentrated fluid, as an oil which does not become crystalline, and when its solution is evaporated, spontaneously or at 212°, an oily mass is also obtained, which does not crystallize from alcohol or æther, or a mixture of these substances. Owing to its occurring only in this amorphous state, I did not attempt to submit it to analysis; but its solution yielded to ammonia a precipitate easily to be recognized as narcotine, by its characters and chemical reactions; and in order fully to substantiate the nature of the base, the hydriodate was converted into a platinum salt in the following manner:—

An aqueous solution was treated successively with nitrate of silver and hydrochloric acid, and bichloride of platinum was finally added to the clear fluid, care being taken to operate with dilute liquids and in the cold, as the platinum compound of narcotine is very prone to change. An amorphous yellow precipitate resulted, which was quickly collected, washed and dried; it gave on ignition a per-centage of 15·88 platinum; 15·81 is that required by the salt of narcotine, whose formula is $C^{46}H^{25}NO^{14}$, HCl, $PtCl^2$.

To the nature of the reaction in this case I would apply the remarks made with reference to papaverine under similar circumstances, but perhaps should not permit the subject to pass without drawing attention to the relation my experiment may bear to a fact made known some time since by Wertheim.

This chemist announced, in a preliminary notice†, that he had detected in opium two new species of "narcotine," which from their composition he named methylo- and propylo-narcotine, while he was led to consider the ordinary alkaloid, hitherto known, as æthylo-narcotine; the whole being derived from one fundamental substance.

* *Loc. cit.* † Chem. Gaz., 1852, p. 36.

I do not think the detailed account of his experiments has yet been published, but it would certainly be interesting to establish the existence of this series in reality, because in that case the ordinary narcotine, with which I worked, would seem to have no longer any replaceable hydrogen, and be the first instance of a natural, or indeed of any compound nitrogenous analogue of ammonium or a metal oxide, unless papaverine be similarly constituted. In the absence of positive proofs, resulting from experiment, nothing can at present be said further as to the nature of these known and unknown bases; but the question seems to me very interesting, and worthy of being settled decisively, Wertheim's being an unsupported statement, particularly as chemically there is nothing to distinguish narcotine and papaverine from other natural alkaloids as a class, or to assimilate them to ammonium.

Behaviour of Cotarnine with Iodide of Æthyle.

Hydriodate of Cotarnine.—Cotarnine is a base derived from narcotine by oxidation; some of it was treated exactly in the manner just described. It was found to be completely converted into an hydriodate, which remained, on distilling off the excess of alcohol and iodide of æthyle, as a red-brown oily mass, highly soluble in hot, insoluble in cold water, and not taking on the crystalline state under any circumstances. This salt was the hydriodate of cotarnine; but being of itself no more fit for analysis than that of narcotine, the composition of the base was ascertained by converting it into a platinum compound, which was a very pale yellow amorphous substance, and gave a per-centage of 22·38 platinum; the formula of the cotarnine salt, $C^{26}H^{13}NO^{6}$, HCl, $PtCl^{2}$, corresponds to 22·57.

This artificial product then comports itself exactly like the alkaloids papaverine and narcotine; and the reaction is no doubt of the same nature.

The formation of these salts of the alkaloids, in cases where water is present, is possibly brought about by a change, observed by Frankland* to take place between iodide of æthyle and water in a sealed tube at 300° F.; the results of this reaction are, according to this chemist, hydriodic acid and æther. It seems not improbable that the presence of a basic substance may determine this decomposition at a much lower temperature.

[To be continued.]

On the Conversion of Thialdine into Leucine. *By* A. Gössmann†.

Cahours was the first to point out the relation between thialdine, $C^{12}H^{13}NS^{4}$, and leucine, $C^{12}H^{13}NO^{4}$, by showing that both have the same atomic composition, but that in thialdine the 4 equivs. of oxygen of leucine are replaced by 4 equivs. of sulphur. Hence it

* Gerhardt Suite de Berzelius, ii. p. 323.

† The fact of this discovery has been already communicated, Chem. Gaz., No. 278, p. 188.

appeared possible that the one substance might be converted into the other, but no experiments have been made with this view. I have found that thialdine may readily be converted into leucine by heating it with water and oxide of silver, the latter becoming converted into sulphuret of silver.

The experiment was performed in the following manner:—Freshly precipitated oxide of silver was introduced with thialdine and a sufficient quantity of water into a glass tube, and this was then heated for three or four hours in boiling water. The fluid filtered from the sulphuret of silver, which still retained an odour of thialdine, was evaporated to the consistence of a syrup, which soon solidified into a crystalline mass. From this, æther only extracted a trace of colouring matter, but hot absolute alcohol dissolved it readily. From this solution leucine was obtained in small white laminar crystals, which were washed with cold alcohol. It had all the properties of ordinary leucine, and was free from sulphur. When heated, it fused, and could be completely sublimed, volatilizing in white fumes. Metallic salts produced no precipitate in its solution.

A second experiment, with oxide of lead, was less satisfactory, on account of the presence of potash, which can scarcely be avoided, and the facility with which leucine combines with oxide of lead.—Liebig's *Annalen*, xc. p. 184.

Observations on the Colouring Matters of Flowers. By E. Filhol.

White Flowers.—If flowers of *Viburnum opulus*, *Philadelphus coronaria*, *Chrysanthemum vulgare*, white roses, and a number of other flowers, be exposed for a few moments to the action of ammonia, they acquire a yellow tinge of greater or less intensity, which remains for a considerable time. Flowers of *Viburnum opulus* by this treatment acquire a yellow colour as fine as that of *Cytisus laburnum*. The matter which thus becomes yellow under the influence of alkalies appears to be present in all white flowers; some flowers contain only a small quantity of it, but these are rare.

In variegated flowers of which the corolla is partially white, these portions usually acquire a fine yellow tint under the influence of ammonia. The stamina, the pistils, and in general all the white parts of flowers, act in the same manner. The leaves themselves become yellow when they are accidentally deprived of chlorophylle. I ascertained this fact with a plant of *Convallaria polygonatum*, of which the leaves presented alternate green and white bands. The latter became bright yellow from the action of ammonia, exactly like flowers. The tissue of some fruits also becomes yellow, although less distinctly, under the influence of alkalies.

The most convenient mode of converting a white flower into a yellow one is to introduce it into a wide-mouthed flask containing a little liquid ammonia, and to expose it to the action of the alkaline vapour. The change then takes place very rapidly. When the greatest part of the flower has become yellow, it may be taken out of the flask and exposed to the air, when the parts which still re-

mained white will gradually change until the flower acquires a uniform tint. The flower may also be dipped into water, alcohol or æther, mixed with a little ammonia. The latter fluids should be preferred when the flower is covered with a fatty coating, which would prevent their being moistened by a watery fluid. If a white flower that has been rendered yellow be dipped into acidulated water, it gradually recovers its white colour.

These experiments remind one that when dyers wish to employ the colour of woad in dyeing, they add a little carbonate of soda to their vat, which gives considerable brightness to the tint. It is easy to prove also that acids, even when very weak, cause the disappearance of the greater part of the colour of a decoction of woad. From this it seems not improbable that the substance which communicates to white flowers the property of becoming yellow when in contact with alkalies may be *luteoline*.

If the petals of white roses be boiled with distilled water, and a little carbonate of soda and sulphate of copper be added to the decoction, as is done with the decoction of woad, a liquid is obtained possessing a bright golden-yellow colour, which may be employed in dyeing yellow. This liquid will give a fine yellow tint to linen and cotton fabrics, and nearly all white flowers will furnish similar results. I have dyed pieces of linen and cotton with decoctions of white roses, of the flowers of *Spiræa filipendula*, *Philadelphus coronaria* and *Galium Mollugo*.

The matter to which white flowers are indebted for this property of acquiring a yellow colour under the influence of alkalies, dissolves readily in water, still more so in alcohol, but less in æther. When the superficial layer of the petals of flowers which have been coloured yellow by ammonia is removed, all the cells are seen to be filled with a yellow fluid, in which no granules are to be perceived.

Dark Red Flowers.—With boiling water or alcohol, the flowers of the wild poppy furnish a violet-red solution. This acquires a fine scarlet colour by the action of acids, even when very weak. If ammonia be poured into the liquid thus acidulated, it becomes of a fine violet colour, without the least mixture of green. But if, instead of adding ammonia to the acidulated liquid, it is added directly to the infusion, this acquires a dirty greenish-red tint. When the flowers themselves are exposed to the action of ammonia, they acquire a fine violet colour, like that obtained with the acidulated fluid. The colouring matter of the poppy therefore differs greatly from the cyanine of MM. Fremy and Cloez, for alkalies do not give it a green colour.

The flowers of *Pelargonium zonale* also become of a fine violet colour under the influence of ammonia; their colouring matter behaves like that of the poppy. The dark red garden verbena gives a violet-red tint to alcohol. The alcoholic solution, treated with ammonia, acquires a vinous colour with a slight greenish tint. If the alcoholic infusion of these flowers be digested with a little dry powdered hydrate of alumina, the latter acquires a light yellow colour, and the supernatant fluid becomes of a fine red colour under the

influence of acids, and of a blue without the least mixture of green by the action of bases. The verbena consequently contains two distinct matters, of which one becomes blue under the influence of bases, whilst the other becomes yellow; it is to the mixture of these two matters that the green colour of the alcoholic tincture of these flowers is due.

The petals of *Anemone hortensis* act like those of the verbena. The flowers of the red pæony become of a pure blue colour under the influence of ammonia. These flowers are rapidly deprived of colour by alcohol; the tincture which they furnish is but slightly coloured, but it becomes of a deep and bright red by the addition of the smallest trace of acid. The acidulated liquid becomes blue with ammonia; whilst the non-acidulated alcoholic solution acquires a greenish tint. The petals of dark red roses become blue when exposed to ammoniacal vapours, but the colour soon passes to a greenish-blue. Alcohol readily dissolves the colouring matter of roses, but acquires very little colour. The slightest addition of acid communicates a deep red colour to the alcoholic solution; ammonia poured into the acidulated liquid changes it to a greenish blue.

Rose-coloured Flowers.—These flowers contain a mixture of two juices, of which one is colourless in acid liquids, whilst the other is red. The former becomes yellow when mixed with alkalies, the second becomes blue, and the mixture of these latter colours produces a green tint. Hence the tints which will be acquired by red or rose-coloured flowers, when exposed to the action of ammoniacal vapours, may be easily indicated beforehand. It is clear that the green colour will approach yellow more and more in proportion to the paleness of the rose, and that it will have a blue tendency in proportion as the colour becomes deeper.

Blue Flowers.—The preceding statements regarding red and rose-coloured flowers applies also to blue flowers. The green colour produced in blue flowers by the action of watery ammonia tends more and more to yellow in proportion to the paleness of the flower.

Effects of the Mixture of the White and coloured Juices of Flowers.—When flowers of iris, of violets, pæonies, of *Cercis siliquastrum*, &c., are infused in alcohol, one is struck with the weakness of tint of the alcoholic solution, even when the petals are completely deprived of colour. It appears natural, at first sight, to attribute this decoloration to the influence of the alcohol, which may act as a reducing agent; but a close examination of the facts does not permit us to rest satisfied with this explanation; and without denying that alcohol may exercise the influence attributed to it by MM. Fremy and Cloez, I think that the following theory, either alone or combined with that just referred to, may readily account for the circumstances in question. In fact, if, instead of treating the above-mentioned flowers with alcohol, they are infused in boiling water, the watery solution is not more deeply coloured than the alcoholic tincture. It would be necessary therefore to admit that water itself is a reducing agent, which is by no means probable.

If into these solutions, whether watery or alcoholic, the smallest

quantity of a soluble acid be poured, they instantly acquire a bright red colour, far deeper in tint than the original liquid. The kind of acid is quite immaterial, for even sulphurous acid immediately brightens the shade, and reproduces the colour which was only concealed. The prolonged action of this acid however soon destroys the colour. Can it be imagined that the colouring matter would reappear immediately upon the addition of *any* acid, if it had been reduced? And especially on this hypothesis, can we account for the action of sulphurous acid? I think not.

In my opinion, the decoloration is due to the mixture of the juice contained in the colourless cells with that of the coloured cells. When alcohol or boiling water acts upon a flower, its organization is destroyed, the juices contained in its cells become mixed, and the colouring matter disappears. The following experiment lends support to this explanation.

If 2 equal volumes of a slightly acidulated infusion, either watery or alcoholic, of pæony flowers be diluted, the one with 4 times its volume of water, the other with 4 times its volume of an infusion of white flowers, it will be seen that the latter will retain much less colour than the former.

The white juices consequently destroy, or rather dissemble the colouring matter. The question now arises, whether these juices act as reducing bodies, or whether they simply form colourless combinations. The experiments to which I have referred above may, I think, serve to answer this question; for if reduction takes place, sulphurous acid would not reproduce the colour. I consider therefore that the colouring matter does not experience any reduction, and that it forms with the elements of the colourless juices a colourless combination. In infusions prepared by the action of alcohol or water upon flowers, one portion of the colouring matter remains free, whilst the other enters into the combination just mentioned. It is easy to separate the coloured portion from the colourless, by triturating the liquid with a little artificial phosphate of lime or dry hydrate of alumina; the coloured part is the first to fix upon the solid body, whilst that of which the colour is dissembled remains for the most part dissolved. If the liquid be filtered, it passes without colour. It may then be coloured red by acid, and green or blue by an alkaline solution.—*Comptes Rendus*, July 24, 1854, p. 194.

On certain Products obtained from Benzonitrile.

By C. W. Bingley, Ph.D., F.C.S.*

By repeated distillations of benzoate of ammonia according to Fehling's method, I procured a quantity of the oil, having the smell of bitter-almond oil, used in perfumery, and by him called benzonitrile, and expressed by the formula $C^{14} H^5 N$. With the intention of separating the phenyle radical, I treated the benzonitrile thus obtained with potassium in equivalent proportions in a sealed tube filled previously with carbonic acid gas. Upon the introduction of

* Communicated by the Author.

the potassium, the benzonitrile assumed a most splendid crimson colour. After subjecting it in the tube to a temperature of 240° Cent. in an oil-bath, a quantity of fine acicular crystals were formed above the oil in the cooler portion of the tube, and on cooling these appeared to be disseminated throughout the whole of the mass in the lower part of the tube. On breaking open the tube, I treated the whole of the contents with water, and filtered, when cyanide of potassium was dissolved out; by distilling the matter remaining on the filter, I obtained a beautiful, bright, green-coloured, oily liquid, smelling somewhat of creosote, and in which the crystals were again apparent. By subsequent treatment with æther and alcohol, and afterwards by sublimation, I obtained these crystals pure and colourless, and found them to be insoluble in æther, alcohol and water. As I am still at present engaged in the research, and have not yet concluded the analyses of these products, I must reserve the subject for a future communication, when I hope to give it more in detail.

Since I have been engaged in the research, I met with Dr. Harley at Giessen, who was at the time there pursuing his researches on the urohæmatine, some particulars of which he published in the Edinburgh Medical Journal; and I may mention the fact, that, with reference to the colour produced by the action of the metallic bases potassium and sodium (similar results have been likewise obtained by me by the use of sodium) upon the benzonitrile, which afterwards, on the oxidation of the metallic base, changes from a splendid crimson colour to a bright green colour, precisely in the same manner that his crimson-coloured substance is changed by baryta to the same bright green colour as mine, there would appear to be some analogy existing between the two substances we have each succeeded in obtaining, and affords some additional hope of the ultimate separation of the phenyle radical.

On Saponine and Senegine. *By* P. A. Bolley.

Bley and Bussy found in the root of *Gypsophila Struthium*, the Egyptian soap-root, a peculiar vegetable matter, which the former called *struthiine*, the latter *saponine*, as it might be supposed to be the same substance which had already been found in the root of *Saponaria officinalis*. Bussy ascertained the composition of this bitter matter. The bitter matter discovered by Gehlen in the root of *Polygala senega*, and called by him *senegine*, has been further investigated by Quevenne, and the admitted analysis of this substance is that of this chemist.

These two bodies (saponine and senegine) are so similar in their physical and chemical properties, that Quevenne was struck by their agreement, although the comparison of some of their reactions led him to the conclusion that they are quite different bodies. He supports his opinion principally upon Bussy's analysis of saponine and his own analysis of senegine. An essential difference is also presented by the behaviour of the two substances with concentrated muriatic acid.

According to Bussy, saponine contains 51·0 per cent. carbon; Quevenne found 55·704 in senegine. Saponine, according to Bussy, contains 7·4 per cent. of hydrogen; senegine, according to Quevenne, 7·529.

I prepared senegine, by Quevenne's prescription, from the officinal extract of senega-root. The process consists in precipitation with acetate of lead, filtration, washing, and decomposition of the precipitate by sulphuretted hydrogen; filtering again, evaporating the filtrate, dissolving it in hot alcohol, and again evaporating; then shaking with æther, dissolving the part insoluble in æther in water, precipitating with basic acetate of lead, filtration, washing, diffusion of the precipitate in water and decomposition by sulphuretted hydrogen, filtration, evaporation, solution in boiling alcohol, and cooling. I obtained a substance agreeing essentially in its chemical behaviour and properties with Quevenne's senegine, except that I never succeeded in obtaining it perfectly white. The powder had always a grayish-yellow tinge, like that of the tannic acid of the oak, and could never be procured quite free from earthy constituents; it was only by repeated solution in hot alcohol and cooling, when the greater part of the substance separates, that I could get the amount of ash down to 1 per cent.

Bussy's saponine was prepared by his very simple process,—the decoction of the finely-divided soap-root with alcohol of spec. grav. 0·848, and filtration whilst hot; the saponine separates on the cooling of the decoction. The substance obtained was perfectly white, but not quite free from ash, although its incombustible constituents were less in quantity than in the substance obtained from the extract of senega.

Both substances possessed the properties generally attributed to them; they were sparingly soluble in cold, but more abundantly in hot water, forming a frothing solution; they dissolved more abundantly in watery than in anhydrous, in hot than in cold alcohol; were insoluble in æther, and destitute of any individual form. Their taste was at first sweetish, then slightly acrid and bitter. They provoke sneezing.

By the combustion of the substance obtained from the senega, I obtained from

I.	II.	III.
0·313	0·276	0·322 grm. dried at 212° F.
0·607	0·537	0·626 grm. carbonic acid.
	0·152	0·180 grm. water;

and by the combustion of the powder procured from the soap-root, from

IV.	V.
0·329	0·313 grm.
0·588	0·557 grm. carbonic acid.
0·204	0·190 grm. water.

This gives for senegine,—

	Found. I.	II.	III.			Calculated.
Carbon	52·83	53·04	53·01	36	216	54·00
Hydrogen ..	..	6·05	6·15	24	24	6·00
Oxygen	..	..	..	20	160	40·00

and for saponine,—

	Found. IV.	V.			Calculated.
Carbon.....	48·64	48·52	36	216	49·54
Hydrogen ..	6·82	6·67	28	28	6·42
Oxygen	..	..	24	192	44·00

The difference in the composition of these bodies consequently lies in the amount of water contained in them.

The formula $C^{35} H^{24} O^{20}$ requires 53·29 per cent. carbon and 6·09 per cent. hydrogen.

The formula $C^{35} H^{28} O^{24}$ requires 48·83 per cent. carbon and 6·51 per cent. hydrogen. These formulæ therefore would at first sight appear to come nearer the analysis. But if we suppose the senegine to contain 1 per cent. of incombustible matter (0·622 grm. gave 0·007 ashes), and bring this into the calculation, the average of the analyses I., II., and III. will rise to 53·6 per cent. carbon, exceeding the amount corresponding with the last-mentioned formula by about 0·3 per cent. The supposition of 36 equivs. of carbon may therefore appear to be more correct.

Even if the formulæ just given agreed with sufficient exactness with the results of the analyses, that they could be regarded as fitted to remove all doubts as to the distinctness of the substances obtained from the two sources above mentioned, I could not attach much weight to them, as it is almost impossible to prepare these non-crystalline substances, which behave with solvents and precipitants exactly like so many other bodies, in a state of absolute purity, and as I certainly had not to do with perfectly pure substance.

On the other hand, however, I believe I have succeeded in showing that the bitter principles of the two roots are one and the same thing, or at all events exhibit no greater differences than those indicated in the above analyses.

By the action of alkalies or dilute acids upon Bussy's saponine, Fremy produced a new acid, which he called *æsculinic acid*, as it is also obtainable from the bitter substance of the horse-chestnut. This, according to him, is a white non-crystalline substance, nearly insoluble in cold water and æther, but soluble in hot water and alcohol, with strong frothing; he found its composition to be,—

Carbon	57·260
Hydrogen	8·352
Oxygen	34·388

I heated a clean watery solution of the bitter matter of senega

with dilute sulphuric acid; after a short time it became turbid from the separation of white flakes; after filtration, washing, which from the gelatinous consistence of the solid body is a troublesome operation, and drying, a powder possessing all the properties of æsculinic acid was obtained. I prepared the same body from the decoction of senega root, with previous separation of the senegine; and lastly, procured it from saponine prepared according to Bussy's process. Its analysis gave,—

	I. From senega.	II. From soap-root.	III.
	0·257	0·2145	0·340 grm.
Carbonic acid	0·557	0·476	0·744
Water.	0·180	0·150	0·232

This gives,—

	Found. I.	II.	III.			Calculated.
Carbon	59·20	60·33	59·72	24	144	59·91
Hydrogen ..	7·70	7·69	7·50	18	18	7·43
Oxygen	33·10	31·98	32·78	10	80	33·46

From these analyses it may safely be admitted that the peculiar principle of senega-root and the Egyptian soap-root is one and the same thing; and notwithstanding the discrepancies between these analyses and Fremy's, it is still extremely probable that his æsculinic acid is nothing but the product of decomposition resulting from the action of dilute acids both upon saponine and senegine. This likewise applies to Quevenne's "acide polygalique modifié," obtained by the action of muriatic acid upon his senegine.

As was to be expected, the action of dilute mineral acids also produced sugar, or at least a sweet hydrate of carbon exhibiting the usual reaction with an alkaline solution of oxide of copper. The product of the decomposition of saponine (and senegine) may be most appropriately named *sapogenine*, by analogy with saligenine.

In the decomposition of saponine, however, we meet with a divergence from the ordinary splitting of bitter matters into sugar and a new product. In saligenine and phloretine the total excess of equivalents of hydrogen over the equivalents of oxygen remains the same as in salicine and phlorizine. But in this case the excess of hydrogen amounts to 4 equivs. in saponine, 8 equivs. in sapogenine. The only way in which we can at present get over this difficulty is to suppose that 2 equivs. of saponine are decomposed, with absorption of water, into 4 equivs. of sugar and 1 equiv. sapogenine:—

4 sugar $= C^{48} H^{40} O^{40}$
1 sapogenine $= C^{24} H^{18} O^{10}$

$$C^{72} H^{58} O^{50} = 2(C^{36} H^{24} O^{20}) + 10HO.$$

I have endeavoured to determine the quantity of hydrate of carbon separated during this decomposition; the results however varied too much to furnish any assistance in the explanation of the reaction.

Saponine, prepared as above from the soap-root, when boiled by itself with an alkaline solution of copper, produces a slight but distinct separation of copper; the substance obtained from senega (perhaps from its mode of preparation) exhibited this reaction very indistinctly. In continuing this investigation, I shall take care to determine the nature of the products of decomposition more exactly; and although the preceding observations have given no reason to suppose that the body called sapogenine is a secondary product, and that a third body is formed with it and the sugar, yet it appears to me that this sapogenine is not quite unchangeable by the further action of the acid and heat; for sometimes it is obtained in opake flakes, which settle readily, and sometimes as a pectine-like, transparent, gelatinous mass. It also appears to acquire more and more of a gelatinous consistence in proportion as the acid is washed out.

Quevenne states that senegine is converted into a gelatinous mass, which may be washed with water, by exposure to the action of strong muriatic acid for twenty-four hours, but that saponine furnishes no similar product. According to my observations, saponine behaves in exactly the same manner. Quevenne also regards the reactions of the alcoholic solution of his modified polygalic acid with metallic salts as characteristic of senegine, and serving to distinguish it from saponine; but the precipitates produced by sapogenine (whether derived from soap-root or senega) are not to be distinguished from each other. Precipitates are obtained with basic acetate of lead, acetate of lead, salts of baryta, peroxide of iron, silver and mercury.

Perhaps it is also worth noticing, whether, as senega is a medicine and very dear at present, soap-root may not be capable of producing the same effects. If the efficacy of this root depends upon the bitter matter, it is very probable that it will be retained by the product of decomposition; at all events this has an intensely acrid bitter taste, which remains long in the mouth. The soap-root furnishes a much larger quantity of this matter than the senega-root, and the pure product is obtained with less trouble.—Liebig's *Annalen*, xc. p. 211.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 15, 1854. (The Earl of Rosse, President, in the Chair.)

"On a New Phosphite of Æthyle," by A. W. Williamson, Ph.D. &c.

The following results were obtained by Mr. Railton in an investigation undertaken in connexion with the idea that the water of constitution discovered by Wurtz may be conceived as basic.

The processes for preparing the compound are thus described by Mr. Railton.

1st. When three atoms of absolute alcohol are acted upon by one atom of PCl^3, this compound is formed. The alcohol is introduced into a retort which is connected with an apparatus for upward distillation, and the retort is surrounded with a freezing mixture. The terchloride is then added drop by drop, the whole is then gently heated for some time, the vapour being allowed to run back into the retort. It is now distilled and the portion which comes off between 140° C. and 196° C. collected and redistilled, that portion being preserved which boils between 188° and 191° C. The quantity of pure æther obtained by this process was not large, and there was left in the retort a considerable amount of PO^3 and other products, which on further heating evolved inflammable phosphuretted hydrogen.

2nd. This æther is obtained with the greatest facility from æthylate of soda and terchloride of phosphorus.

I introduce into a thirty ounce stoppered retort about a pint of æther, which must be perfectly free from alcohol and from water. The æthylate of soda is then added, and as much PCl^3 is taken as is necessary to form chloride of sodium and phosphite of æthyle. The æther is absolutely necessary, for without it, the action of the PCl^3 is so violent, as to set fire to the æthylate.

The PCl^3 is introduced into the mixture of æther and æthylate of soda through a long funnel, which is drawn to an extremely fine point, by which means it enters drop by drop into the mixture, thus avoiding the violent action which otherwise occurs.

The retort should be kept quite cool and frequently shaken. If these precautions are neglected considerable loss is experienced.

When the whole of the PCl^3 has been added, the æther is distilled off by a water-bath. The retort is then transferred to an oil-bath which is gradually heated up to about 240° C. The whole of the distillate obtained by the oil-bath is collected in a dry receiver, and as it is prone to decomposition if distilled in air, it is distilled in an atmosphere of hydrogen, the portion which comes off at 188° C. is the phosphite of æthyle. I may here notice the remarkable fact, that this substance has two boiling-points, as doubtless have many other bodies, if distilled under similar circumstances. In air it boils at 191° C., while, as I said before, it boils in hydrogen at 188° C. Its specific gravity is 1·075.

3rd. The reaction which occurs on the formation of this æther may be represented by the following formula:—

$$3NaO,\ C^4H^5O + PCl^3 = 3NaCl + 3C^4H^5O,\ PO^3.$$

The carbon and hydrogen were estimated in the usual manner by oxide of copper, the phosphorus as follows. A weighed portion of the æther was introduced into a twelve ounce stoppered bottle; concentrated nitric acid was poured upon it, and the bottle allowed to stand in a warm place, loosely stopped, for several days. When nitrous fumes no longer appeared, the oxidation of the phosphorous

acid was deemed to be complete. The acid liquid was then saturated with ammonia, some chloride of ammonium and sulphate of magnesia then added, and the mixture well shaken. It was allowed to stand for some time, when a precipitate of phosphate of magnesia and ammonia was formed; this was washed, dried, and ignited, and the amount of phosphorus calculated from the result. These are the results.

Grms.		CO^2	HO	$2MgO, PO^5$
·2405	æther gave	·3784	and ·1920	,,
·5115	,,	·8047	and ·4155	,,
·4513	,,	,,	,,	·302
·4110	,,	,,	,,	·278

From these results the following per-centages are calculated.

	Required.	Found.	
C^{12}	43·11	42·91	42·89
H^{15}	8·98	8·87	9·03
P	19·16	18·92	19·10
O^6	28·75	29·30	28·98
	100·00	100·00	100·00

These results being satisfactory as regards the formula, the density of the vapour was then ascertained and found to be in strict accordance with theory. The method of taking the vapour densities of bodies liable to oxidation was described by me about twelve months ago, in the Chemical Society's Quarterly Journal. It was used in the following experiments.

1st. Weight of globe filled with air at 53° F. and 30·2 in. barometer, 188·213 grs.

Weight of empty globe, 186·313 grs.

Weight of globe and vapour at 521° F. and 30·3 in. barometer, 192·387 grs.

Capacity of globe at 60° F., 6·00 cub. in.

Residual hydrogen ·05 cub. in.

Capacity of globe at 521° F., 6·40 cub. in.

Six cubic inches of air at 53° F. and 30·2 in. barometer, become at 60° F. and 30 in. barometer 6·12 cub. in., and weigh 1·90 gr.

·05 cub. in. hydrogen at 60° F. become ·094 cub. in. at 521° F., and weigh ·002 gr.

6·40 − ·094 = 6·306 cub. in. vapour at 521° F., which at 60° F. and 30 in. barometer = 3·376 cub. in.

Hence 192·387 − ·002 = 192·385 − 186·313 = 6·072 grains, the weight of 3·376 cub. in. vapour.

100 cubic inches.. = 179·86 grs.
100 cubic inches air = 31·01 grs.

The density is therefore 5·800, from which it appears that its combining measure is four volumes.

Density by calculation $=5{\cdot}763$.

A second experiment gave $5{\cdot}877$.

This substance has a highly offensive odour, it burns with a bluish white flame, is soluble in water, alcohol, and æther, and is slowly decomposed in contact with air.

On boiling phosphite of æthyle with concentrated solution of baryta, in water, it is decomposed into alcohol and a salt which varies according to the amount of baryta used. If one atom of the æther be treated with one of baryta, a crystallized salt is produced on evaporation, the carbon and hydrogen in which are, according to an analysis I have just completed,—

	Found.	Required.
Carbon	20·354	24·158
Hydrogen ..	5·356	5·050
Baryta	36·880	37·090

In that marked 'required' I have supposed the salt to bear the following formula and to be completely anhydrous, $2C^4H^5O, BaO, PO^3$, but if we suppose that four atoms of water are present in the salt analysed, the relation will stand thus :

Found.	Required.
20·354	20·453
5·356	5·540

The formula would then be $2C^4H^5O, BaO, PO^3+4HO$.

When two atoms of baryta are made to act upon one atom of the æther, a salt is obtained which does not crystallize, and it may be evaporated in air without sensible decomposition. This salt is perfectly neutral to test paper; when dry it is a white friable deliquescent mass, the formula of which will be $C^4H^5O, 2BaO, PO^3$. If an excess of baryta is used, a white salt is thrown down on boiling, which I suppose to be $HO, 2BaO, PO^3$.

I have prepared another compound with three equivalents of amyle. This was obtained from amylate of soda by an analogous process to that described for the phosphite of æthyle.

Analysis has pointed out the formula $3C^{10}H^{11}O, PO^3$. Like phosphite of æthyle it is easily decomposed on being heated in air; heated in hydrogen it is more stable and then boils at 236° C. It is soluble in æther and in alcohol, but only slightly soluble in water.

"On some new derivatives of Chloroform," by A. W. Williamson, Ph.D. &c.

According to the results of recent researches in the constitution of salts and the methods thence introduced of explaining chemical reactions, it is equally correct to represent such a reaction as that of hydrochloric acid on hydrate of potash, as consisting in an exchange of hydrogen of the one for potassium of the other, or of chlorine in one for peroxide of hydrogen in the other. In Mr. Kay's researches as described in the following brief outline, this notion has obtained

very striking illustration; for he has obtained a peculiar body in which the chlorine of chloroform is replaced by peroxide of æthyle by the action of chloroform on three atoms of æthylate of sodium, which product may be equally well conceived to be a body in which the hydrogen of three atoms of alcohol is replaced by the tribasic radical of chloroform.

According to the older theories of the capacity of saturation of salts, this compound would contain a tribasic modification of formic acid, for it has the same relation to formic æther as a so-called tribasic phosphate has to a monobasic one.

To one equivalent of chloroform were added, by degrees, three equivalents of dry and powdered æthylate of soda, a violent action taking place with the evolution of much heat; the liquid was entirely distilled from the residue (chloride of sodium) by means of an oil-bath, and then subjected to a series of fractional distillations, which yielded a small distillate between 50° and 60° C., smelling strongly of vinous æther, a large distillate (about three-fourths of the whole) between 77° and 78° C., which was chiefly alcohol, and another small distillate (about one-sixth) between 145° and 145°·3 C.

The distillates obtained by the above process, except that of alcohol, being small, the following modification was adopted.

Sodium was dissolved in absolute alcohol until the action became feeble, chloroform was then added, care being taken to keep the liquid alkaline; more sodium was then added, and the process repeated several times, until the chloride of sodium precipitated became very bulky. The liquid was then distilled off and chloroform added to the residue, and also distilled off. To this first distillate sodium was again added, and treated with the last distillate instead of pure chloroform, the same precautions being used as before. This method gave similar distillates, and in about the same proportion as that first used; the highest distillate however boiled constantly at 146° instead of at 145°·3 C.

This compound which boils at 145° to 146° C. is a colourless limpid liquid, only slightly soluble in water, having a strongly aromatic odour, readily inflammable and burning without much smoke; its specific gravity is ·8964; it remained liquid at 0° F.

Several analyses made of this body agree in giving to it the formula $C^7 H^{16} O^3$, which would also be the empirical formula of a tribasic formic-æther; the density of its vapour also corresponds very closely with the same formula.

Pentachloride of phosphorus added to a portion of the compound produced a heavy liquid having the odour of chloroform.

A small quantity of the body was dissolved in alcohol, distilled upwards for two or three hours with solid hydrate of potash and then distilled off; the residue was next dissolved in water and made exactly neutral by hydrochloric acid, filtered to remove the turbidity, and then a few drops of chloride of mercury added; after a little time and by the application of heat, a very slight precipitate of subchloride of mercury was formed; also the colour of sesquichloride of

iron was a little darkened by another portion of the solution, thus showing that the action of potash on the compound had produced formic acid, but in very small quantity.

An equivalent of dry hydrochloric acid was passed into a portion of the compound; the gas was wholly absorbed, a considerable amount of heat being evolved and the liquid assuming a brownish colour; the liquid after the absorption of the gas still remained perfectly neutral. It was next distilled with the thermometer: it began to boil at 20° C. and rose gradually to 100°; it was collected in three portions, the first (about one-sixth of the whole) passing over between 20° and 50°, the second (about one-third) between 50° and 68°, the third (one-half) between 68° and 100°. I was unable to carry these distillations further in consequence of the small quantity of the liquid available.

Two equivalents of dry hydrochloric acid were passed into a larger quantity of the compound; towards the close the gas was absorbed less freely, a portion passing through; after this treatment, the liquid fumed and was highly acid; it was distilled upwards for some time by which a portion of free hydrochloric acid was expelled, and then distilled fractionally; about one-third came over between 56° and 60° C., one-fourth between 60° and 70°, one-sixth between 70° and 80°, and the remainder (about one-fourth) between 80° and 88°. To the lowest distillate about an equal bulk of water was added; the substance floated on the surface and seemed to be little, if at all dissolved by the water; a sufficient quantity of carbonate of soda was next added to neutralize the free acid, and the liquid pipetted from the water, it was then distilled upwards for some time with dry chloride of calcium, and afterwards distilled off; this distillate was found to boil constantly at 55°·5 C. An analysis made of this body agrees closely with the formula $C^6 H^{14} O^5$.

The distillate which came over between 60° and 70° after being treated in the same way as the lower distillate, also yielded a liquid which boiled at 56° C.

As both methods hitherto used for the purpose of obtaining the body $C^7 H^{16} O^3$ afforded only small quantities, the treatment of chloroform with an alcoholic solution of potash was tried; for this purpose 12 oz. of solid hydrate of potash and 20 oz. of quicklime were added to about three pints of absolute alcohol, and the alcohol distilled upwards for six or seven hours; 6 oz. of chloroform were then added gradually, the upward distillation being continued about two hours longer; the liquid was next distilled off to dryness by means of an oil-bath, and submitted to fractional distillation; by this method a much larger quantity of the compound was obtained than by the former processes; it was found to boil constantly at 146° C., and its analysis agreed almost exactly with the formula. In this process the lowest distillate had the same smell of vinous æther which was before observed in the other methods.

An attempt was made to produce the intermediate compounds $C H Cl^2$, AeO, and C H Cl, 2AeO, by adding dry and powdered æthylate of soda very gradually to a large excess of chloroform; but

the liquid after being separated from the precipitate, was found, on distilling fractionally, to resolve itself into chloroform, alcohol, and the body ($C^7 H^{16} O^3$) already obtained, the presence of no other substance being observable.

With a view of obtaining a compound analogous to the body $C^7 H^{16} O^3$, in which amyle should be introduced instead of æthyle, dry amylate of soda was prepared, to three equivalents of which one equivalent of chloroform was added, the liquid separated from the precipitate and then distilled fractionally; a large proportion of fusil-oil was obtained, together with a small proportion of a body which boiled at a high temperature,—from 260° to 290° C., but chiefly from 260° to 270°; the purification of this substance was not carried further, as at each distillation a considerable portion was decomposed even in an atmosphere of hydrogen, the small quantity of the liquid available precluding any more attempts at distillation.

"Note on Nitro-glycerine," by A. W. Williamson, Ph.D., Professor of Practical Chemistry in University College, F.C.S.,

This compound is formed by acting upon glycerine with a mixture, in equal volumes, of concentrated nitric and sulphuric acids, the glycerine being added by a few drops at a time.

It is heavier than water, in which it is slightly soluble, and is soluble in alcohol and in æther.

From its proneness to decomposition in drying, even by the air-pump, a complete analysis could not be made, but a qualitative examination of the relative amounts of carbon and nitrogen gave the following results:—

	1.	2.	3.	4.
Volumes of mixed gases	101	91·5	99	97
Volumes of nitrogen not absorbed by potash	32	30·5	34	33
Carbonic acid absorbed by potash	69	61	65	64

	1.	2.	3.	4.	5.
Mixed gases	178	194	173	194	192
Nitrogen	61	66	58	65	65
CO^2	117	128	115	129	127

From these results the following formula was deduced:—

$$C^6 H^8 O^6 + 3NO^5 = C^6 \begin{matrix} H^5 \\ 3NO^4 \end{matrix} O^6 + 3HO.$$

It would therefore appear that 3H are replaced by $3NO_4$.

On boiling this compound with concentrated solution of potash, it is decomposed into glycerine and nitrate of potash.

THE CHEMICAL GAZETTE.

No. CCLXXXVI.—September 15, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of the Halogen Compounds of Æthyle and Amyle on some Vegetable Alkaloids. *By* Mr. HENRY HOW, Assistant to Professor Anderson, Glasgow University.

[Continued from page 325.]

On Strychnine.

HAVING examined the action of the alcohol iodides on a number of bases with only 1 equiv. of nitrogen, I was anxious to ascertain the deportment of a base containing, like strychnine, 2 atoms of this element, in the hope of throwing some light on the function of the second equivalent. The researches of Hofmann, on a great variety of alkaloids, have shown us that the volatile bases, starting from the original type ammonia, and passing upwards to the most complicated substances, may be viewed as nitrogen attached to basic hydrogen alone, or to it in combination with hydrocarbons performing its functions, or finally to hydrocarbons occupying the entire hydrogen part of the molecule. In the fixed vegetable alkaloids, we see oxygen also included in the system; and if, as I have attempted to prove in the case of some of these, they are comparable with nitryle bases, the hydrogen part of the compounds must contain oxygenized hydrocarbons acting as hydrogen. In the case of a base containing 2 atoms of nitrogen, it is possible that this element performs as it were two parts; one may be referable to the function of that in any ammonia, amidogen or nitryle base, while the other may be more analogous to that property in virtue of which, in combination with oxygen, as NO^4, it replaces an atom of hydrogen in the carbohydrogen forming part of the compound molecule. The possibility of the latter being the case, as regards one of the atoms of nitrogen in an alkaloid containing two, was thrown out as a speculative suggestion some few years ago by Fresenius.

In the hope of arriving at some conclusions regarding these points, I proceeded to examine the deportment of strychnine with reagents suited to my purpose. The decision of the whole question seems to devolve upon the reactions of two classes of agents; the amount of basic hydrogen would be learned by the quantity of hydrocarbons of alcohol radicals the base is capable of taking up from their halogen compounds, while reducing agents should remove oxygen from

any oxidized combination of nitrogen; if it be as NO^4 that the second atom of this element exists, sulphuretted hydrogen should, as in other compounds of this class, remove the 4 equivs. of oxygen, and permit 2 additional atoms of hydrogen to enter into the new product.

The first part of the question is gone into in some detail in the present memoir, while, without being in a position to give anything decisive at present with regard to the second, I may mention that strychnine undergoes a curious decomposition in contact with sulphide of ammonium, which results in the formation of hyposulphite of the base itself—a very beautiful and stable salt—and the production of another substance I am still engaged in studying. The description of the properties and composition of these products I must reserve till I am able to show the complete history of the change, and how far the real constitution of strychnine is determined by the experiments; but I may state, that, from what I have as yet learned, the decomposition does not appear to be of the nature just spoken of.

Action of Iodide of Æthyle on Strychnine.

Hydriodate of Æthylostrychnine.—Strychnine, in a state of fine powder, is readily attacked by iodide of æthyle; even when these two substances are boiled together in water, a perceptible quantity of iodine is found in the solution, precipitable by silver salts; the insolubility of the alkaloid, however, no doubt interferes with the reaction, for the change is much more easily effected when spirit of wine is used as a medium. The most successful method I found to be that employed before, viz. to operate with alcohol and iodide of æthyle on the powdered base in sealed tubes; at the temperature of boiling water the change is complete in about twenty minutes. A heavy crystalline powder is formed, differing in appearance from strychnine; but solution is not at any time during the experiment complete, no change being perceptible beyond the more definitely crystallized nature of the solid contents of the tube, the complete solubility of which in boiling water announces the completion of the reaction.

A boiling aqueous solution of the new substance having deposited upon cooling masses of silky-white crystals, which proved to consist of an hydriodate, they were collected, washed, and a portion of them, dried at 212° F., was submitted to analysis in the ordinary way, with the following results:—

Carbon	56·27	46	= 276	56·31
Hydrogen.....	5·60	27	27	5·50
Nitrogen	..	2	28	5·71
Oxygen.....	..	4	32	6·55
Iodine	25·98	1	127·1	25·93

A comparison of the above results and appended calculation will show that a replacement of hydrogen by æthyle in, or an attachment

of iodide of æthyle to, the alkaloid has taken place, according to the equation,—

$$\underbrace{C^{42}\,H^{22}\,N^{2}\,O^{4}}_{\text{Strychnine.}} + C^{4}\,H^{5}\,I = \underbrace{C^{42}\left\{\begin{matrix}H^{21}\\C^{4}\,H^{5}\end{matrix}\right\}N^{2}O^{4},\,HI = C^{46}H^{27}\,N^{2}\,O^{4}\,I}_{\text{New salt.}}.$$

The salt crystallizes without water, and whatever constitution subsequent experiment may assign to it, it will be now described as an hydriodate, and its base as æthylostrychnine.

Hydriodate of æthylostrychnine is soluble in about 50 or 60 parts boiling water, and in about 170 of water at 60°; a tolerably dilute fluid deposits the salt in very fine, white, four-sided prisms of considerable lustre, which they retain in the dry state; it is also soluble in rectified spirit, and comes out of that menstruum in short prismatic crystals. It is unaltered in the air; at 212° it loses no weight, but acquires a slight shade of colour; at a higher temperature it fuses and blackens, affording thick vapours of an alkaline reaction and disagreeable odour; and a yellowish sublimate, rather oily in appearance, forms on the sides of the vessel; no vapours of iodine are to be observed during the process of heating.

This salt gives no base with potash or ammonia, but is less soluble in these alkaline fluids than in water, and is consequently precipitated, on their addition, in strong solutions; strong potash throws it down at once in the cold, and when ammonia is added to a concentrated boiling aqueous solution, the unchanged salt deposits immediately in fine needles. It is readily decomposed by oxide of silver, and the hydrated base may be obtained in the crystalline state. These reactions assimilate the salt to an iodide rather than to an hydriodate, and the characters of the base, when isolated as far as it can be, being those of an analogue of ammonium oxide, its salts would perhaps be more correctly called iodide, chloride, &c., and in the following pages I make use of these terms, without however making any alteration in the conventional nomenclature for the base.

The salts of æthylostrychnine generally are characterized by their beautifully crystalline nature, and the facility with which they may be obtained pure. I have analysed a few, as affording a favourable opportunity of examining the combinations of one of these derivatives from a natural fixed alkaloid.

Nitrate of Æthylostrychnine.—This compound is readily formed by double decomposition from the preceding, by use of nitrate of silver in warm dilute solutions. It is easily soluble in boiling water, but of extremely sparing solubility in this menstruum when cold; so much so, that I have used this property as a test of the existence of the base on many occasions; a solution containing it, even when tolerably dilute, depositing, on the addition of a little nitric acid, in a short time, very fine, four-sided, prismatic crystals; in more concentrated fluids their appearance is immediate. The salt, in a pure state, is in colourless prisms of high refractive power, which may be obtained of great beauty from dilute aqueous fluids. Its analysis gave the following results:—

Carbon	64·60	46 =	276	64·94
Hydrogen	6·53	27	27	6·35
Nitrogen	..	3	42	9·88
Oxygen	..	10	80	18·83

which agree precisely with the formula $C^{46}H^{26}N^{2}O^{4}$, HO, NO^{5} = $C^{46}H^{27}N^{2}O^{4}NO^{6}$. Its crystals contain no water.

Chromates of Æthylostrychnine.—Both neutral and acid chromate of potash yield precipitates with salts of the base; the former giving, even in dilute fluids, short, prismatic, yellow crystals, and the latter tufts of silky needles. As the number of bichromates, of whose analysis we are in possession, is in reality very small, being limited, I believe, to those of potash and ammonia, whose constitution is peculiar, I examined the salt in the present instance, to see if it were quite analogous to these compounds, which it does not appear to be.

Bichromate of æthylostrychnine is deposited from strong mixed solutions of the appropriate salts in very beautiful transparent plates of a golden-yellow colour; it falls, as just mentioned, from more dilute fluids, in tufts of needles; it is readily soluble in boiling water, but when cold this liquid dissolves but little of the salt. Dried at 212° F., it furnished,—

Carbon	57·15	..	46 =	276	57·33
Hydrogen	5·91	..	28	28	5·81
Nitrogen	..	..	2	28	5·81
Oxygen	..	..	6	48	29·99
Chromic acid	20·86	20·88	3	101·4	21·06

which gives results according satisfactorily with a formula which contains an atom of water more than those of the corresponding potash and ammonia salts, and may be thus written:—

$C^{46}H^{26}N^{2}O^{4}$ HO, CrO^{3}, $HOCrO^{3}$ = $C^{46}H^{27}N^{2}O^{4}CrO^{4}$, $HCrO^{4}$.

The failure of the analogy here, with the peculiar combinations of potash and ammonia, is worthy of attention; of course, it readily admits of explanation, if the 1 atom of water be assumed as retained from the water of crystallization of the new salt. The loss sustained by exposing the crystals to 212° was 3·43 to 3·77 per cent.; 3·60 is the calculated per-centage corresponding to a loss of 2 atoms of water by a salt of the formula $C^{46}H^{27}N^{2}O^{4}CrO^{4}$, $HCrO^{4}$ + 2Aq.

Platinum Salt of Æthylostrychnine.—By the successive addition of nitrate of silver and hydrochloric acid to a warm solution of the iodide, and that of bichloride of platinum to the clear fluid, this salt fell as a curdy yellow precipitate, which became crystalline after some hours; from more dilute liquids it crystallizes at once in a very beautiful form, namely, in groups of stars, of which the individual rays resemble, on being magnified, the fronds of some species of ferns. It furnished 17·46 per cent. platinum. The formula $C^{46}H^{27}N^{2}O^{4}Cl$, $PtCl^{2}$ requires 17·37. The salt is anhydrous when crystallized.

The substitution of terchloride of gold for the platinum solution gives, by the same process, a yellowish curdy precipitate, soluble in

boiling water; and this fluid deposits colourless brilliant prisms of splendid appearance, of the corresponding gold compound.

The chloride is a very soluble salt, crystallizing in needles; the sulphate is less soluble, an acid fluid furnishing groups of pearly needles and flakes, possibly a bisulphate; the oxalate, prepared in a similar manner, has much the same appearance; the acetate remains as a gummy transparent mass when a proper solution is evaporated to dryness at 212°; the chloride gives, with mercuric chloride, a curdy white precipitate, crystallizable from hot water in white needles.

Carbonates of Æthylostrychnine.—Having observed, in the course of experiments to be detailed presently, which were made for the purpose of obtaining the æthylostrychnine in an isolated state for analysis, the tendency of the base, when free and in solution, to absorb carbonic acid, it occurred to me to attempt the production of any carbonates of determinate composition it might be capable of forming. I shall be able to show that the base enters readily into combination with this acid, forming at least two salts, of which while the one, the monocarbonate, cannot be obtained in the dry state, the other, a bicarbonate,—into which, with the occurrence of some other product of decomposition, the first appears to have a great tendency to pass,—may be readily procured in the solid form, of determinate composition, and even as a very beautiful crystalline substance.

It was found that when moist carbonate of silver is added to iodide of æthylostrychnine, covered with a little water, double decomposition ensues, and is complete in a few minutes, when the vessel containing the mixture is well shaken; iodide of silver, of course, remaining undissolved, while the fluid contains a carbonate of extreme solubility. When, without employing heat, the process is quickly performed, so as to occupy only a few minutes of time, a perfectly colourless liquid is obtained; but with a longer contact of the excess of carbonate of silver, or the application of heat, the fluid assumes a light claret colour, which, by the continued action of either of the above causes, may be deepened almost indefinitely, and seems to be the result of oxidation. This solution shows all the characters of a carbonate in its reactions, and when saturated with dilute nitric acid, becomes filled, almost before the cessation of effervescence, with the characteristic crystals of the nitrate of æthylostrychnine; when evaporated to dryness, however, either *in vacuo* or at 212° F., it is found to have undergone a singular decomposition. The residue obtained in both cases is crystalline, and in part colourless, with claret-coloured spots pervading its mass; on adding water to this, the great bulk dissolves to a deep claret-coloured fluid, which contains carbonic acid and æthylostrychnine, while an amorphous substance, in whitish flocks, remains in appreciable quantity.

It is obvious that, with the observation of this decomposition, all hope of analysing the expected residue of pure monocarbonate of æthylostrychnine was at an end; nevertheless, as I was curious to know the actual amount of carbonic acid retained, a certain weight

of the residue, obtained by evaporation *in vacuo*, was treated with cold water, and to the filtered solution was added a mixture of chloride of barium and caustic ammonia, which had been suffered to remain in contact for some time; the precipitate produced would contain all the carbonic acid, and when collected and washed with the proper precautions, it was ignited; the resulting per-centage, calculated on the amount of residue employed, was almost that of the bicarbonate to be described immediately.

The flocky matter remaining undissolved by the water appears to be a new base; it does not effervesce with acids, but dissolves tranquilly and completely, and is again thrown down by ammonia in white flocks; with nitric acid it yields no crystalline salt, as æthylostrychnine does; it dissolves with the greatest ease in spirits of wine, but is not to be obtained from this menstruum in a crystalline state; the solution, which is, or soon becomes of a fine pink colour, deposits no crystals on standing for weeks even, but red transparent drops appear at the sides and bottom of the vessel, and an amorphous residue remains on evaporating the fluid to dryness; these characters evidently separate the product widely from strychnine and æthylostrychnine, and must cause it to be considered a peculiar base. It would be an interesting decomposition to follow out, but I had far too little substance at my command to do more than observe the above facts at the time, and the consumption of material necessary for its investigation is an obstacle to the research.

Bicarbonate of Æthylostrychnine.—The preceding experiment having shown the tendency of the base to accumulate carbonic acid, I proceeded to seek a higher carbonate, by passing a stream of the washed acid gas into the solution obtained by the double decomposition just mentioned. During this process a very slight turbidity ensued; and after the gas had passed through the fluid a considerable time, this was filtered, and obtained perfectly colourless; it proved to admit of evaporation to dryness, *in vacuo* or at 212°, with similar results as to the properties and composition of the residue. In the former case, a white crystalline mass, having however here and there faintly claret-coloured spots, remains, which by continued drying becomes a white enamel-like substance; the latter process yields a crystalline residue of a reddish-yellow colour; these products are the bicarbonate. The salt undergoes in a very slight degree the decomposition before spoken of, but this is scarcely perceptible when evaporation is quickly performed; the flocky base produced, at 212° especially, being exceedingly minute in quantity.

The aqueous solution of the bicarbonate,—and, though not deliquescent, the salt is extremely soluble in water,—has a powerful alkaline reaction, and proves a ready means of forming the compounds too soluble to be got by double decomposition. The dry salt dissolves completely in a little absolute alcohol; the addition of good æther to this fluid causes in a little time the deposition of bicarbonate in very fine, colourless, prismatic crystals, of great refractive power. In the analyses which follow, the carbonic acid

was estimated as before mentioned, and the specimens were of different preparation:—

Carbon	..	..	46 =	276	65·09
Hydrogen	..	..	28	28	6·60
Nitrogen	..	..	2	28	6·60
Oxygen	..	..	6	48	11·34
Carbonic acid	10·62	10·44	2	44	10·37

These numbers agree perfectly with those required theoretically by a salt of the base analogous to bicarbonate of potash, as expressed in the formula $C^{46}\,H^{26}\,N^{2}\,O^{4}\,HOCO^{3}$, $HOCO^{3}=C^{47}\,H^{27}\,N^{2}\,O^{4}\,CO^{3}$, HCO^{3}. This salt is somewhat interesting, inasmuch as it is, I think, the first combination of one of the artificial ammonium bases with carbonic acid which has proved definite by analysis. While on the subject, it will not be out of place to mention some experiments made with the natural alkaloids, for the purpose of preparing, if possible, similar salts with these bodies, as it gives the opportunity of correcting an error to be found in the manuals. Thus it is stated in Liebig's 'Traité*,' that a carbonate of strychnine is obtained both by precipitation of its salts with carbonated alkalies and solution of the base itself in water, through which a stream of carbonic acid gas is passed, it being deposited in this case in beautiful crystals. I have carefully gone over those experiments, and satisfied myself that the substance in both cases is the pure base. A carbonate is certainly obtained by double decomposition, between hydrochlorate of strychnine and carbonate of silver; but it exists only for a short time, even in solution, as the gas escapes on standing, and the pure alkaloid is deposited in fine, though small crystals.

I could obtain no dry carbonates of morphine, codeine, papaverine or narcotine; they behave like strychnine under the same circumstances. While these experiments were in progress, my attention was called to the production of a definite carbonate of quinine by Langlois†, and I gave up the idea I had entertained of extending the observations to the vegetable alkaloids generally, as it is possible the subject will be gone into at greater length by this chemist.

Hydrate of Æthylostrychnine.—I have mentioned already that potash and ammonia fail to separate this base from its iodine combination, which is thrown down unaltered from its aqueous solution by strong potash, and is also less soluble in ammoniacal than in pure water. Oxide of silver readily effects the elimination of the iodine; in fact, when the solid salt is covered by moist oxide of silver, a few minutes' contact in the cold suffices to complete the change, iodide of silver remaining undissolved, and a fluid of a red purple colour being formed, which contains all the base. When this is suffered to evaporate to dryness spontaneously, a crystalline purplish mass results, which contains some carbonic acid, and dissolves in a small quantity of cold water, leaving however constantly a minute residue of the nature before spoken of in describing the monocarbonate.

* Liebig. Traité de Chimie Organique, par Gerhardt, ii. p. 630.
† Chem. Gaz., 1853, p. 470.

Evaporation *in vacuo* over sulphuric acid produces a less crystalline residue, of a similar colour, which is found to be completely soluble in hot absolute alcohol to a purple fluid; a concentrated solution of this kind deposited on cooling a substance in colourless, small, prismatic crystals. These were collected on a filter, washed from the coloured mother-liquor with a little absolute alcohol and æther, and finally dried out of contact of air. Tests, to be mentioned presently, having shown the deposit to be, as nearly as it is possible to be procured, the pure base, it was retained *in vacuo* till it ceased to lose weight, and then gave these results on analysis:—

Carbon.....	68·13	46 =	276	67·81
Hydrogen	8·19	31	31	7·61
Nitrogen	..	2	28	6·87
Oxygen.....	..	9	72	17·71

I must mention that the complete desiccation of this substance was extremely tedious, occupying above a fortnight, and that in the state in which it was burned it was a very light and bulky powder, highly electrical and hygroscopic, so that the high per-centage of hydrogen is not remarkable. The numerical results of the above analysis admit of translation into the formula, which, in analogy with the corresponding combination of potash, the assumed congener of æthylostrychnine, may be written $\dot{C}^{46}\,H^{27}\,N^{2}\,O^{4}\,O, HO + 3Aq$; and this hydrate of oxide of æthylostrychnine differs from the known crystallized hydrate of potash in containing an atom of water less.

The substance as analysed was not deliquescent; it dissolved immediately on being covered with cold water, furnishing a red fluid, and leaving only a minute flocky residue, which seemed to increase on application of heat; the solution, made in the cold, became filled, almost immediately on the addition of a little nitric acid, with the crystalline salt before spoken of as characteristic of the base, and no effervescence was perceptible.

When the hydrate, carefully dried *in vacuo*, is dissolved in a quantity of absolute alcohol, sufficient to prevent a deposit on cooling, the addition of some æther causes the formation of a tremulous jelly, which renders the whole fluid semi-solid. On stirring for some time with a glass rod, this jelly gradually changes into a crystalline substance; by management of the respective amounts of alcohol and æther, very beautiful small crystals, perfectly colourless, may be obtained at once, or on standing. To effect this result, the hydrate must be well dried, or it falls in purple oily drops.

The hydrate cannot be freed of its water of crystallization by exposure to 212°, as at this temperature it undergoes decomposition in a much greater degree; a portion so heated was found to effervesce in a lively manner with acids, and though it yielded plenty of the crystalline nitrate, yet when treated with cold water it left a considerable residue of the character already described. I made an analysis of a part of the substance, giving these reactions with a view of ascertaining how far decomposition had proceeded, and give it with the understanding of its approximative value:—

Carbon	69·77	46 =	276	69·34
Hydrogen.....	7·85	30	30	7·53
Nitrogen	..	2	28	7·05
Oxygen.....	..	8	64	16·08

These numbers agree closely with the formula $C^{46} H^{27} N^2 O^4 O, HO + 2Aq$, containing an atom of water less than the preceding; and it is just possible that the errors occasioned by the presence of carbonic acid and the basic product of decomposition, both of which, after all, bear but a small proportion to the whole substance, may counterbalance each other; I leave the fact of the analysis, since it is some sort of control over that immediately preceding.

A freshly prepared solution of the base, by action of oxide of silver on the iodide, has a red-purple colour and an extremely bitter taste; its reaction is highly alkaline. It yields no immediate precipitate with solutions of barium and calcium chlorides, but causes partial precipitation on application of heat; it throws down from sulphate of magnesia, in the cold, a flocky precipitate, and also gives with solutions of the heavy metallic oxides and with alumina immediate deposits; but I had not material sufficient to determine its solvent power in particular cases. On being boiled, it evolves the odour of a volatile base. With chlorine, bromine, and iodine it yields products. When it, or its carbonate, is treated with hydrosulphuric acid, and suffered to stand, a hyposulphite is found to result, which may be obtained crystalline by evaporation, and is soluble in alcohol. This base gives the same reaction as strychnine with sulphuric acid and chromate of potash.

When iodide of æthylostrychnine is heated in a retort with excess of soda-lime, a heavy oil distils over, which is partly basic and partly insoluble in acids. The hydrochloric solution of the soluble portion gave with bichloride of platinum an uncrystalline salt; but I had not sufficient to determine if, in this decomposition, the æthyle molecule attaches itself to the volatile base, which is no doubt either leucoline or æthyloleucoline.

Action of Iodide of Æthyle on Æthylostrychnine.—This reaction appears to result in the formation of iodide of æthylostrychnine and some other product. I employed for the experiment the mother-liquor of the hydrate which was analysed; this alcoholic fluid was sealed up in a tube with iodide of æthyle, and the whole was heated for half an hour in boiling water. The liquid remained clear while hot, but soon became turbid on cooling, and finally deposited some rounded, transparent, yellowish grains. These proved, when separated from the mother-liquor by decantation, to be completely soluble in hot water; their solution deposited a little flocky matter, and when filtered from this and evaporated, groups of stellate crystals. These crystals agreed in characters with iodide of æthylostrychnine, and furnished with oxide of silver a caustic yellow liquor, which became filled with prismatic crystals on the addition of a little nitric acid. The alkaline solution had not, it is true, the rich red-purple afforded in former instances, but in all other characters was quite the same.

The mother-liquor of the grains, when distilled to a syrup, and, after the addition of some water, finally evaporated to dryness, left a red and green resinous residue, which dissolved incompletely in hot water; the aqueous solution again left a resin, only partially soluble, on evaporation; there exists in this solution a base, partially, at least, precipitable by ammonia as an iodine compound. It is possible this secondary product may somewhat affect the characters of the iodide of æthylostrychnine, which, I think, is certainly formed, as might have been expected.

[To be continued.]

On an Anhydrous Persulphate of Iron.

By PETER HART, of Manchester*.

A short time ago, I had put into my hands, by the workman who attends to the platinum-concentrating retort at the vitriol manufactory to which I am attached, a few crystals and a small quantity of a curious granular powder, both of a pinkish-white colour, which he had found in the retort after it had stood to cool for some days when full of vitriol. The total quantity of substance, which had before made its appearance at long intervals, was very small. The powder, viewed through a lens, was perfectly crystalline; on drying it became of a pale straw-colour, the pink hue being again regained on exposure to the air; at the same time the powder became sensibly damp. On continued exposure for several days, it first became covered with numerous cauliflower-like excrescences, and eventually formed a yellow pasty mass. It was very slowly soluble in water, for I washed the powder repeatedly with it, in order to get rid of the large quantity of free acid at first adhering to it. After it had attained the pasty consistency by exposure as above, it was easily soluble. I was at first much afraid it would turn out to be a salt of platinum, the result of some action on the retort; and I was agreeably surprised to find that it did not contain a trace of platinum, but was simply a sulphate of the peroxide of iron. For some time I was at a loss to account for its presence. The conclusion I eventually came to was the following:—The leaden pans in which the acid is concentrated preparatory to being run into the retort, are covered over with sheet lead, which is supported on iron rods; these are sheathed with lead, and are laid across the pans; this leaden coating is gradually destroyed by the acid vapours evolved, which lay bare the iron, which is then easily acted upon by the gas, and forms small masses of an iron salt, which eventually drop off and are dissolved in the acid undergoing concentration; this acid, with the iron in solution, when further concentrated, deposits on cooling the salt in question. In order to satisfy myself of the correctness of this view, I boiled a quantity of the strongest sulphuric acid in a large flask, dropping in powdered protosulphate of iron until it ceased to be dissolved; I then set the whole on one side until cold, when I

* Communicated by the Author.

found a quantity of very minute crystalline scales had collected at the bottom; the large excess of acid was poured off, and they were washed with water until the washings ceased to taste acid; they were then dried as much as possible between folds of bibulous paper, and a weighed quantity placed over sulphuric acid to dry at the ordinary temperature. When dry, they had the same yellow appearance as they present when dried at a high temperature. As the salt originally found in the still contained a quantity of dirt, which rendered it unfit to be employed in a quantitative determination, I proceeded to analyse the salt, prepared as before stated, as follows:— Having first satisfied myself that it was not a double salt, and did not contain a trace either of *protosulphate* or any other salt of iron, in short, that it was absolutely pure persulphate of iron, I took a weighed quantity in a porcelain capsule, and heated it first to 212°; after continuing at this heat a sufficient time, it was weighed, the loss indicating the water present; it was then heated to a bright red heat until it was perfectly decomposed, the expulsion of the sulphuric acid being aided by the occasional introduction of fragments of carbonate of ammonia; when perfectly decomposed, it was again weighed, the difference between this weighing and the last being the weight of sulphuric acid driven off; the substance remaining in the crucible was pure peroxide of iron, which, as it retained the shining scaly form of the original salt, had a very pretty appearance. The following is the result of the analysis placed beside the theoretical numbers:—

Analysis of 14·71 *grs.*

	Found.	Calculated.
Water	0·13	0·00
Fe^2O^3	5·74	5·88
SO^3	8·84	8·83
	14·71	14·71

It will be observed that I have obtained some water in this analysis, but this is owing to my not having dried it sufficiently over sulphuric acid. The analysis evidently proves it to be an anhydrous persulphate of iron. I have been induced to write this account of it by finding that in all the works on chemistry on which I have been able to lay my hands, there is no description of this salt as I have found it, the nearest approach being in Brande's 'Manual of Chemistry,' where, speaking of persulphate of iron, he says,— "When concentrated sulphuric acid is dropped into a strong solution of this persulphate," that is, a solution of persulphate formed by oxidizing the protosulphate with nitric acid, "it throws it down as a white anhydrous powder; this occasionally occurs in sulphuric acid of commerce, and has been mistaken for sulphate of lead;" but here he does not mention the existence of this salt, at once *anhydrous and crystallized.*

In the method of preparing the salt which I have given, the following must be the reaction which takes place:—

$$2(FeO+SO^3)+2(SO^3)=Fe^2O^3+3SO^3+SO^2.$$

On a New Series of Metallic Radicals. *By* J. Bouis.

In studying the action of the alkaline metals upon the hydrochloric æther of caprylene, I have shown that a liquid was obtained in the cold, the composition of which agreed with the formula $C^{16}H^{17}$, indicating that the hydrochloric æther has lost chlorine to furnish a compound, which may be considered as the radical $\left\{\begin{matrix}C^{16}H^{17}\\C^{16}H^{17}\end{matrix}\right\}$, or as a mixture of hydruret of capryle and caprylene, resulting from its splitting,—

$$2C^{16}H^{17} = \underset{\text{Caprylé.}}{C^{32}H^{34}} = \underset{\text{Hydruret of caprylé.}}{C^{16}H^{18}} + \underset{\text{Caprylene.}}{C^{16}H^{16}}.$$

The reaction is very different in operating by heat. When sodium is heated with hydrochloric æther, the metal acquires a violet tint, and swells up considerably; the temperature rises, and evolution of hydrogen takes place; the fine purple-violet colour disappears, the sodium being converted into chloride, which absorbing the liquid, forms a pasty mass. To do away with this inconvenience, a series of communicating retorts may be employed, with some fragments of sodium in each; the hydrochloric æther is then put into the upper retort and heated, when the reaction becomes very brisk; the violet substance first formed disappears, and the liquid arriving less impregnated with chlorine in the other retorts, produces the violet compound with great rapidity. The liquid obtained is pure caprylene.

The violet substance may be very well preserved in caprylene or oil of naphtha; water, alcohol, and oxygenated liquids in general decompose it. When pressed between paper and exposed to the air, it becomes white; soda and chloride of sodium are formed. Hydrochloric æther in great excess decomposes it; chlorine also destroys it. When thrown into water, it is violently decomposed. Drying *in vacuo* gives it a brighter tint. When calcined, it evolves much hydrogen, and leaves a residue of charcoal, containing sodium in a very divided state. All these properties would agree well with a subchloride, and such was my first opinion; but I have in vain attempted to arrive at the same result with different carburets of hydrogen, such as benzine, oil of naphtha, naphthaline, &c. It may, on the other hand, be regarded as a chloride combined with the carburet $C^{16}H^{16}$, in which some hydrogen might be replaced by its metallic equivalent, thus: $\left\{\begin{matrix}C^{16}H^{15}\\Na\end{matrix}\right\}ClNa$. And this view is supported by the following reactions:—

The violet compound is formed by treating chlorocaprylic æther with sodium; and this would tend to lead us to the supposition that a body of the nature of the metallic radicals is produced, such as $\left(\begin{matrix}C^{4}H^{5}\\M\end{matrix}\right)Cl$, $\left(\begin{matrix}C^{10}H^{11}\\M\end{matrix}\right)Cl$, &c., and consequently represented by $\left(\begin{matrix}C^{16}H^{17}\\M\end{matrix}\right)Cl$.

But this hypothesis cannot be admitted, because we produce the same compound directly with the carburet, $C^{16}H^{16}$. Thus when caprylene, $C^{16}H^{16}$, is heated with sodium, no action takes place; but if dry chlorine be introduced, the violet compound immediately makes its appearance. I have prepared this substance by boiling the carburet, $C^{16}H^{16}$, over sodium, and passing a current of dry chlorine into the liquid; the violet substance is then very abundant, and if the sodium be in excess, a liquid remains possessing the properties and composition of caprylene. A disengagement of hydrogen takes place, arising either from the compound formed, or from the decomposition by the metal of the hydrochloric acid formed at the expense of the carburet of hydrogen:—

$$C^{16}H^{16}+2Na+Cl=\begin{pmatrix}C^{16}H^{15}\\Na\end{pmatrix}ClNa+H.$$

Experiment proves therefore that a carburet enters into the composition of the body containing less hydrogen than capryle, and it shows also that this carburet must be $C^{16}H^{16}$.

Oil of naphtha, or any other hydrocarbon, in contact with sodium and chlorine, produces nothing but chloride of sodium; the addition of a few drops of caprylene gives the substance a violet colour. The carburet of hydrogen, $C^{16}H^{16}$, treated with chlorine so as to furnish products of substitution, diluted with oil of naphtha and heated with sodium, does not produce the reaction indicated unless some non-modified carburet, $C^{16}H^{16}$, be added.

The presence of chlorine and caprylene being indispensable for the formation of the violet body, I prepare the latter by means of caprylene to which a few drops of chlorocaprylic æther have been added, or simply of the product of the action of chlorine upon caprylene; the reaction is thus regulated, and as soon as it commences the fluid is stirred with a rod to divide the sodium. Prepared in this manner, the violet substance may be dried at 266° F. *in vacuo* without decomposition; but when exposed to the air several times, it took fire, probably in consequence of the presence of minute particles of sodium, to which also the disengagement of hydrogen on contact with water may be attributable.

When decomposed by water, the violet body produces an evolution of hydrogen, and furnishes soda, chloride of sodium and a liquid which is lighter than water and has the properties of caprylene. The difficulty of purifying this compound, and freeing it from the excess of chloride of sodium, or sodium, has prevented me hitherto from making an exact analysis of it. The following is the method to which I had recourse. The substance, dried in the tube in which it was produced, is decomposed by water; the hydrogen is measured, the soda obtained by an alkalimetric process, and the chlorine determined in the form of chloride of silver. The proportion of hydrogen was always less than corresponded with the sodium of the soda, and this circumstance would tend to confirm my opinion that the hydrogen is entirely due to the mechanically interposed sodium. Ac-

cording to the probable composition of the compound, we should have,—

$$\begin{pmatrix} C^{16} H^{15} \\ Na^2 \end{pmatrix} Cl + HO = C^{16} H^{16} + NaO + ClNa.$$

Chlorocaprylic æther, heated with sodium in a closed tube, furnished the same violet compound. All that has been said regarding hydrochloric æther may apply equally to the hydriodic and hydrobromic æthers, or simply to iodine and bromine.

The carburet, $C^{16} H^{16}$, dissolves iodine very readily, with a bright red colour, a reaction perhaps more sensitive than chloroform or sulphuret of carbon for the detection of very small quantities of iodine. This solution, treated with sodium, gives a bright blue compound, analogous to the preceding.

The action of bromine upon caprylene is very energetic; each drop that falls into the liquid produces a hissing and projection; the liquid remains colourless. The best mode of using bromine is to dissolve it in oil of naphtha, and to add this solution, in small portions, to the caprylene heated with sodium. The product thus obtained is of a very fine deep blue colour. These compounds will be represented by,—

$$\begin{pmatrix} C^{16} H^{15} \\ Na^2 \end{pmatrix} I, \quad \begin{pmatrix} C^{16} H^{15} \\ Na^2 \end{pmatrix} Br.$$

Different carburets of hydrogen, such as benzine, oil of naphtha, naphthaline, &c., having only given negative results, I have thought that it would not be uninteresting to examine the corresponding æthers of the other series. I tried the chloramylic and chloracetylic æthers; but as they attack sodium too rapidly, I operated with the intervention of pure oil of naphtha, which by itself has no action. These two æthers furnished compounds analogous to those obtained with caprylene. The chloracetylic æther must be gently heated, and the sodium then well stirred; the blue matter is formed on cooling.

If the sodium be replaced by potassium in these experiments, the colours produced are magnificent; but the reaction is so rapid that I was unable to arrest it, and consequently could not preserve the substances formed.

I am now engaged in the production and study of the compounds formed by the simultaneous action of sodium and chlorine, bromine and iodine, upon the carbonated hydrogens homologous with olefiant gas; and if my experiments confirm the views put forth above, we shall obtain a new series of organic metallic radicals, constituted by the carburet $C^m H^m$, and in which one or more equivs. of hydrogen may be replaced by a metal:—

$$\left\{ \begin{matrix} C^m H^{m-1} \\ \\ M \\ \\ M \end{matrix} \right\} \begin{matrix} Cl \ldots\ldots \\ or \\ Br \ldots\ldots \\ or \\ I \ldots\ldots \end{matrix} \left\{ \begin{matrix} C^m H^{m-x} \\ \\ M^x \\ \\ M \end{matrix} \right\} \begin{matrix} Cl \\ or \\ Br \\ or \\ I. \end{matrix}$$

Comptes Rendus, August 7, 1854, p. 288.

Researches in Organic Chemistry. By A. Cahours.

I. *On Caprylia.*

By distilling castor-oil with a concentrated solution of caustic potash, M. Bouis discovered a peculiar alcohol, which stands in the same relation to caprylic acid as vinic alcohol to acetic acid, or the alcohol obtained by the distillation of wood to formic acid. By the careful examination of this new product, M. Bouis has succeeded in obtaining a certain number of compounds, corresponding with the ætherial compounds furnished by ordinary alcohol. The beautiful researches of M. Wurtz show, that to each alcohol there is a corresponding volatile alkali derived from ammonia; thus,—

Methylic alcohol,	$C^2\ H^4\ O^2$,	corresponds to methylia,	$C^2\ H^5\ N$
Vinic alcohol,	$C^4\ H^6\ O^2$,	corresponds to æthylia,	$C^4\ H^7\ N$
Propionic alcohol,	$C^6\ H^8\ O^2$,	corresponds to propylia,	$C^6\ H^9\ N$
Butyric alcohol,	$C^8\ H^{10}\ O^2$,	corresponds to butyria,	$C^8\ H^{11}\ N$
Amylic alcohol,	$C^{10}\ H^{12}\ O^2$,	corresponds to amylia,	$C^{10}\ H^{13}\ N$

So that the alcohol of M. Bouis, $C^{16}\ H^{18}\ O^2$, ought to correspond to caprylia, $C^{16}\ H^{19}\ O^2$.

This supposition has been fully confirmed by experiments. By heating in sealed tubes, hydriodate of caprylic æther, with a solution of ammoniacal gas in concentrated alcohol, I obtained a compound which crystallized in large plates, which were very soluble in water, especially when hot. The solution was decomposed by potash, when an oily matter separated, possessing very distinct basic properties. Dried over solid potash and purified by distillation, this substance presented the following properties.

It is a very limpid colourless oil, endowed with an ammoniacal odour, which also resembles in some degree the odour of mushrooms. This oil is lighter than water, and boils at a temperature of 341°·6 to 347° F. Its analysis and the density of its vapour have led me to attribute to it the formula $C^{16}\ H^{19}\ N$, which corresponds with 4 vols. of vapour.

This body dissolves readily in muriatic acid, with which it forms a deliquescent compound, crystallizing in broad pearly laminæ. If a solution of bichloride of platinum be poured into a concentrated solution of this salt, an abundant yellow precipitate, of a crystalline appearance, is formed; this dissolves readily in boiling water, and is deposited, on the cooling of the liquid, in the form of brilliant lamellæ, of a fine golden-yellow colour, resembling iodide of lead.

Sulphuric and nitric acids also form crystallizable combinations, which are very soluble in water.

This substance becomes heated by contact with chlorides of benzoyle and cumyle, and furnishes compounds corresponding to benzamide and cuminamide. This new base, for which the name of *caprylia* is proposed, therefore presents the most manifest analogies with its homologues,—methylia, æthylia, &c. By the action of iodide of æthyle upon it, imidogen and nitryle bases are obtained, as with the analogous compounds.

I have analysed caprylia and some of its compounds; these analyses have given me the following results:—

$C^{16}H^{19}N$ ..... caprylia.
$C^{16}H^{19}N, ClH$ ..... hydrochlorate of caprylia.
$C^{16}H^{19}N, ClH, PtCl^2$ ..... platinochlorate of caprylia.
$C^{16}H^{19}N, IH$ ..... hydriodate of caprylia.
$C^{16}H^{19}N, SO^3, HO$ ..... sulphate of caprylia.
$C^{16}H^{18}N, IH, (C^4H^5)$ ..... hydriodate of caprylic æthyle.

II. *On Methylosalicylic Æther.*

Ten years ago* I pointed out that the Gaultheria oil of commerce is a compound æther of the wood-spirit series, the methylosalicylic æther, which may be obtained artificially by the action of a mixture of sulphuric and salicylic acids upon wood-spirit. This compound, like the analogous vinosalicylic æther, possesses the property of forming with bases definite and crystallizable compounds, in opposition to the general rule amongst the compound æthers. To explain this singular anomaly, M. Gerhardt has invented an exceedingly ingenious hypothesis as to the constitution of these æthers, derived from the constitution which he assigns to the hydrated acids. According to M. Gerhardt, a hydrated acid may be regarded as water, $\left.\begin{matrix}H\\H\end{matrix}\right\}O^2$, in which 1 molecule of hydrogen is replaced by a molecule of a binary, ternary or quaternary group. Upon this hypothesis, the composition of hydrated salicylic acid would be expressed by the formula—

$$\left.\begin{matrix}C^{14}H^5O^4\\H\end{matrix}\right\}O^2;$$

that of the anhydrous acid by the formula—

$$\left.\begin{matrix}C^{14}H^5O^4\\C^{14}H^5O^4\end{matrix}\right\}O^2.$$

If we now admit the introduction of methyle into the group salicyle, $C^{14}H^5O^4$, the constitution of the oil of Gaultheria must be represented by the formula—

$$\left.\begin{matrix}C^{14}H^4(C^2H^3)O^4\\H\end{matrix}\right\}O^2;$$

consequently the second molecule of hydrogen, remaining intact as in hydrated salicylic acid, will of course play the same part.

Starting from this point, M. Gerhardt has substituted for the second molecule of hydrogen a molecule of benzoyle, cumyle or succinyle, by the action of methylosalicylic æther upon the chlorides of those radicals. Hence it appeared that we ought also to be able to replace this molecule of hydrogen by methyle, æthyle and amyle. I succeeded in obtaining this result by the action of methylohydriodic, æthylohydriodic, and amylohydriodic æthers upon methylo-

* Chem. Gaz., vol. i. p. 365.

salicylate of potash in sealed tubes; in this manner I procured perfectly neutral compounds, no longer forming combinations with potash, and becoming decomposed by the action of this base, with reproduction of salicylic acid. These new compounds, which may be represented by the following formulæ,

$$\left.\begin{matrix}C^{14}H^{4}(C^{2}H^{3})O^{4}\\(C^{2}H^{5})\end{matrix}\right\}O^{2},\quad \left.\begin{matrix}C^{14}H^{4}(C^{2}H^{3})O^{4}\\(C^{4}H^{5})\end{matrix}\right\}O^{2},\quad \left.\begin{matrix}C^{14}H^{4}(C^{2}H^{3})O^{4}\\(C^{10}H\ )\end{matrix}\right\}O^{2},$$

furnish definite crystallizable compounds with chlorine, bromine and fuming nitric acid. The first of these bodies boils at 478° F., the second at 504° F., and the third above 572° F.

By substituting æthylosalicylate of potash for the methylosalicylate of the same base, a series of analogous compounds, which may be represented by exactly similar formulæ, are obtained. The true methylo-, æthylo- and amylosalicylic æthers,

$$\left.\begin{matrix}C^{14}H^{5}O^{4}\\C^{2}H^{3}\end{matrix}\right\}O^{2},\quad \left.\begin{matrix}C^{14}H^{5}O^{4}\\C^{4}H^{5}\end{matrix}\right\}O^{2},\quad \text{and}\quad \left.\begin{matrix}C^{14}H^{5}O^{4}\\C^{10}H^{11}\end{matrix}\right\}O^{2},$$

are consequently still to be discovered.

I may add, in conclusion, that by the reaction of chloride of acetyle upon hydrate of phenyle, a volatile and very stable liquid is obtained, without decomposition, which, under the influence of potash and a high temperature, reproduces hydrate of phenyle and acetic acid. The chlorides of amanthyle, capryle, and pelargyle furnish similar results. These reactions may be formulized in the following manner:—

$$C^{12}H^{6}O^{2}+C^{4}H^{3}ClO^{2}=ClH+C^{16}H^{8}O^{4},$$
$$C^{12}H^{6}O^{2}+C^{14}H^{13}ClO^{2}=ClH+C^{26}H^{18}O^{4},$$
$$C^{12}H^{6}O^{2}+C^{16}H^{5}ClO^{2}=ClH+C^{28}H^{20}O^{4},$$
$$C^{12}H^{6}O^{2}+C^{18}H^{17}ClO^{2}=ClH+C^{30}H^{22}O^{4}.$$

Comptes Rendus, July 31, 1854, p. 254.

On an advantageous Method of preparing Peroxide of Lead. By F. Wöhler.

A solution of acetate of lead is precipitated by carbonate of soda, and chlorine gas passed into the thin pasty mass thus obtained until all the carbonate of lead is converted into brown peroxide, which is then filtered and washed. In this manner all the oxide of lead is converted into peroxide, and no chloride of lead is formed; chloride of sodium remains in solution, and acetic acid and carbonic acid are set free. The proportions are:—3 parts of crystallized carbonate of soda to 4 parts of crystallized acetate of lead; it is better however to employ a slight excess of the former, in order to make sure of preventing the formation of chloride of lead. From 4 parts of acetate of lead 2½ parts of peroxide are obtained, whilst 4 parts of

minium scarcely furnish 1½ part. The peroxide thus prepared instantly becomes white in sulphurous acid gas, and then incandescent. It is especially applicable to this instructive lecture-experiment.—Liebig's *Annalen*, xc. p. 383.

ANALYTICAL CHEMISTRY.

Note upon some little-known Reactions of Boracic Acid.
By C. TISSIER.

I. *Boracic Acid and Protoxides.*

Lime.—Hydrated lime dissolves very readily in a boiling solution of boracic acid; the quantity of crystallized acid required to effect complete solution is 25 or 30 times the weight of lime.

Magnesia.—The hydrocarbonate of magnesia is the salt most readily dissolved by the acid; calcined magnesia long resists its action.

Protoxides of Iron and Manganese.—These two bases (hydrated) dissolve very easily in a boiling solution of boracic acid. A large proportion of the acid is required, 25 to 30 parts by weight for the protoxide of manganese, and 50 to 60 times for the protoxide of iron. The solution of the acid protoborate of manganese appears to be unalterable in the air; that of the iron salt, on the contrary, immediately becomes turbid, depositing sesquioxide of iron.

Protoxide of Zinc.—This oxide dissolves in a boiling solution, even after it has been calcined at a red heat; the proportion of acid necessary for its solution is the same as with protoxide of iron.

II. *Boracic Acid and Sesquioxides.*

Alumina and Sesquioxide of Iron.—Solution of boracic acid does not dissolve the least trace of either of these oxides, either when acting directly upon the hydrated oxides, or by the double decomposition of one of their salts with borate of soda in presence of an excess of boracic acid.

III. *Boracic Acid and Anhydrous Carbonates.*

Carbonates of Baryta and Lime.—Boracic acid has little or no action upon these bodies.

Carbonate of Magnesia.—The acid has no action upon anhydrous carbonate of magnesia.

IV. *Boracic Acid and Insoluble Phosphates.*

Phosphate of Lime.—The action of boracic acid upon this salt is exceedingly interesting.

If to an acid solution (muriatic or nitric) containing phosphate of

lime (or a soluble phosphate and chloride of calcium) and an excess of boracic acid, borate of soda be added in sufficient quantity to saturate the acid holding the phosphate in solution, no borate of lime is precipitated, while all the phosphoric acid is thrown down in the form of phosphate of lime. The phosphate of lime thus precipitated has not a variable composition like that precipitated by saturating with ammonia, but it has a constant composition and a well-defined formula. It corresponds with that for which Berzelius gives the formula $8CaO, 3PO^5$, and which contains, calculating with the equivalents at present admitted,—

Phosphoric acid	49·09
Lime	50·91

This mode of precipitating phosphoric acid from its solution, with the process which I laid before the Academy last year for the separation of this acid from alumina and sesquioxide of iron, will greatly facilitate the determination of the quantity of phosphates contained in soils, manures, &c.—*Comptes Rendus*, July 24, 1854, p. 192.

On the Determination of Potato-starch mixed with Wheat-starch. *By* M. Cailletet.

A given weight of the starch to be tested is suspended in a known volume of watery solution of potash in a graduated burette. A known quantity of an alcoholic solution of bromine is then added; in a short time a precipitate is formed, of which the volume is to be noted. Now as the very different volumes of the precipitates formed under the same circumstances by pure wheat-starch and by starch mixed with one-fourth of potato-starch are well known, it is easy, by a simple arithmetical operation, to determine the proportion of potato-starch in the sample under examination.—*Comptes Rendus*, July 31, 1854, p. 246.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Electro-chemical Treatment of Ores of Silver, Lead and Copper. *By* M. Becquerel.

The electro-chemical process consists in preparing the ores in such a manner that the resulting compounds of silver and lead (in operating upon galena) may be soluble in a saturated solution of common salt; these compounds are chloride of silver and sulphate of lead. When the solution is made, it is put into a wooden reser-

voir, when the decomposition of the metallic salts is effected with couples formed of plates of zinc and tinned iron or copper, of masses of calcined charcoal, or even of plates of lead and the same negative elements. The plates of zinc or lead are placed in bags of sail-cloth filled with saturated solution of salt, which are immersed in the metallic solution; the other plates are put into the latter, and the communication established between them by means of wires. With plates of zinc a deposit of very fine particles of all the reducible metals is obtained on the negative plates; with lead plates the deposit consists of silver of greater or less purity according to the proportion of lead in the solution. Wooden boxes, of a few millimeters in thickness, steamed for the removal of soluble extractive matters, are better than the sail-cloth bags; or porous earthen vessels may be employed, filled with fragments of amalgamated zinc and mercury. The action is then more regular, and the quantity of zinc consumed is in atomic proportion with that of the deposited metals. By varying the constitution of the voltaic couples, each of the metals contained in the solution may be successively separated.

Experiments have been made upon quantities of ore varying from 100 grms. to 100 kilogrms.; the quantities of silver collected in twenty-four hours varied from a few decigrammes to 1 or 2 kilogrms. In general the operation was completed in about four-and-twenty hours; but with the assistance of a separate battery, of which the temperature was raised by means of steam, about a fourth of the time was saved. This battery is of course united voltaically to the other apparatus, and in this case the latter consists only of lead plates, of which some form the positive, others the negative elements of the pile; and although the lead acts directly upon the chloride of silver, the two opposite currents resulting from this action do not appear to injure the effect of the independent battery. This method combines the advantages of the direct precipitation of silver by the lead and those resulting from the action of the separate battery, which converts each apparatus into a voltaic couple. When lead plates are employed, the fluid after several operations contains chloride and sulphate of lead, which are decomposed by lime.

The lead deposited on the negative elements is in very fine particles or in a spongy form; after being washed and pressed together, it is melted in earthen crucibles, covered on the surface with powdered charcoal to prevent oxidation; several hundred kilogrammes of lead have been fused in this manner. This precipitated lead is pyrophorous; it must not therefore be exposed to the air in drying, as in this case it would become oxidized with disengagement of heat. It is then in a most favourable state for the production of white lead.

The process has been tried on a large scale by M. Duport Saint-Clair, a Mexican silver refiner; and he considers it to be applicable to the working of silver ores, not only in case of a positive want of mercury, but even when the price of that metal becomes rather high.—*Comptes Rendus*, June 26, 1854, p. 1095.

THE CHEMICAL GAZETTE.

No. CCLXXXVII.—October 2, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On two Processes for the Preparation of Aluminium, and on a new form of Silicium. *By* H. St. Claire Deville.

The present notice forms the continuation of an investigation undertaken in a purely scientific view, but the result of which, confirmed by fresh experiments, leads me to the conclusion previously announced, that aluminium, which constitutes as much as 25 per cent. of the most ordinary clays, is destined to become a most valuable metal for useful purposes. Medallions of a large size, which I have had struck, the blades which I place before the Academy, have experienced no alteration in the air; small ingots, which have been handled every day for several months, have lost none of their brilliancy. Lastly, this substance is unoxidizable to such a degree, that it resists the action of the air in a muffle heated to the temperature required for assays of gold; in the cupel the lead burns away, the litharge fuses by the side of the aluminium, which loses none of its properties. If this metal formed an alloy with lead, it might evidently be cupelled.

Aluminium conducts electricity eight times better than iron, consequently as well as, and perhaps better than, silver.

The place which must be assigned to aluminium among the metals, to remain faithful to the principles of classification of M. Thenard, must remove it from magnesium, zinc and manganese, by the side of which it at present is arranged; it must form the type of a very natural group, consisting with it of chromium, iron, nickel and cobalt. They have a character in common, to which I attach, in a theoretical point of view, the highest importance; they are not attacked by dilute or concentrated nitric acid, in which they acquire the *passive* state. This passivity, which is very energetic in the case of aluminium and chromium, the protoxides of which (if aluminium possess one) have but an ephemeral existence, becomes manifest in the case of iron only in the presence of concentrated nitric acid, in which the production of protoxide is impossible; it is only feebly evident in nickel and cobalt, the sesquioxides of which are unstable, and only enter into combination with difficulty: these two metals form the passage to manganese. I shall on some future occasion return to these analogies, which furnish a new idea of the nature of this passivity, at least of the chemical part of the phænomenon.

Like iron, aluminium does not form an alloy with mercury, and scarcely takes up a trace of lead; with copper it furnishes alloys, which are light, exceedingly hard and very white, even when the copper constitutes 25 per cent. of the mixture. It is characterized in the highest degree by the property of forming with carbon, and especially with silicium, a gray *fonte*, which is granular, brittle, and crystallizes with remarkable facility; the planes of cleavage intersect at apparently right angles.

When this *fonte* is acted upon by hydrochloric acid, the hydrogen, by its disagreeable odour, indicates the presence of carbon; but what it especially contains is silicium, which separates in a pure state when the action of the boiling concentrated hydrochloric acid is continued for some time. It appears to me evident that the silicium exists in the cast aluminium in the same state as the carbon in gray cast iron, a state still little known, and upon which my investigations relative to aluminium will, I trust, throw some light.

This silicium is in brilliant metallic plates, perfectly similar to platinum filings, and in this form it differs essentially from the silicium of Berzelius. I do not however believe silicium to be a true metal; on the contrary, I am of opinion that this new form of silicium is to ordinary silicium what graphite is to carbon. With the most perfect inalterability, it possesses all the chemical properties which Berzelius attributes to the residue of the imperfect combustion of ordinary silicium. To give an idea of this indifference to the action of the most powerful reagents, I may state that the new silicium has been exposed to a white heat in a current of pure oxygen without experiencing any change in weight, that it has resisted the action of hydrofluoric acid, and dissolves solely in a kind of *aqua regia*, formed of hydrofluoric and nitric acids. Potash in a state of fusion converts it into silica, but the operation is a very long one. It conducts electricity like graphite.

The cast aluminium from which I extract the silicium contains more than 10 per cent. of it. It appears to be requisite for the production of this *fonte* that the silicium be in the nascent state at the moment of the combination, for the aluminium fused in an earthen crucible attacks its sides *, sets the silicium free, but does not unite with it; the metal retains its malleability, and the crucible contains a chocolate powder nearly identical with the silicium of Berzelius. It will be seen subsequently that this *fonte* is the first product which results from the action of the battery on the chloride of aluminium and chloride of silicium, which always exist together in the impure substances submitted to decomposition.

I shall describe two methods of preparation, the only ones with which I am well acquainted, and which I have frequently put into practice:—

1. *Process by Sodium.*—From 200 to 300 grms. of chloride of aluminium are placed in a large glass tube of a diameter of 3 to 4 centims., and well isolated between two plugs of asbestos. A current

* I now prepare infusible crucibles, which are not liable to attack, with calcined alumina rendered plastic by means of gelatinous alumina.

of hydrogen, carefully dried and free from air, is passed through one end of the tube. The chloride of aluminium is then heated in this current of gas, so as to expel the hydrochloric acid, chloride of silicium, and the chloride of sulphur with which it is always impregnated. Some glass trays, as large as possible, and containing each one several grammes of sodium, previously broken into small pieces between two dry sheets of filtering paper, are then introduced into the tube. The tube being filled with hydrogen, the sodium is fused, the chloride of aluminium is heated, distils over, and is decomposed with an incandescence which is moderated so as to avoid it altogether if desirable. The operation is complete when the whole of the sodium has disappeared, and the chloride of sodium formed has absorbed so much chloride of aluminium as to be completely saturated; the aluminium is then surrounded by a double chloride of aluminium and sodium, which is a very fusible and volatile compound. The trays are then removed from the glass tube, and placed in a large porcelain tube provided with a receiver, and a current of dry hydrogen free from air passed over it. It is now heated to a bright red, when the chloride of aluminium and sodium distils over without decomposition, and after the operation the whole of the aluminium will be found, collected into one or two large globules at the most, in each tray. They are washed in water, which removes a little salt with an acid reaction and some brown silicium. To form all these globules into one ingot, they are placed, after being cleaned and dried, in a porcelain capsule containing as flux a little of the distilled product of the preceding operation, *i. e.* of the double chloride of aluminium and sodium. The crucible being heated in a muffle to a temperature near the fusing-point of silver, all the globules unite into a brilliant ingot, which is allowed to cool, and washed. The metal must, lastly, be kept fused in a covered porcelain crucible until all the vapours of chloride of aluminium and sodium, with which the metal always remains impregnated, have disappeared. The ingot of metal is found enveloped in a light pellicle of alumina, arising from the partial decomposition of the flux.

It will be imagined that the sodium may be replaced by its vapour, which is so easily produced, so as to obtain aluminium in an œconomic manner, even by employing an alkaline reducing agent. But I shall return hereafter to the modification of the apparatus just described, necessary to render this mode of fabrication practicable.

2. *By the Battery.*—It has hitherto appeared to me to be impossible to obtain aluminium by the pile in watery fluids. I should have believed this impossibility to be absolute, if the brilliant experiments of M. Bunsen did not shake my conviction. Nevertheless I must say that all the processes of this kind which have been published recently have not given me any result.

It is by means of the double chloride of aluminium and sodium ($Al^2 Cl^3$, NaCl)*, of which I have already spoken, that this decom-

* This interesting substance, which represents spinel with a soda base in which the oxygen is replaced by chlorine, is the type of a great number of analogous bodies, which I am studying at this moment, in order to compare them

position is effected. The aluminium bath is prepared by taking 2 parts by weight of chloride of aluminium, and adding to it 1 part of dry pulverized chloride of sodium. The whole is mixed in a porcelain capsule, heated to about 392° F. The combination soon takes place with evolution of heat, and a liquid is obtained which is very fluid at 392° F., but not volatile at that temperature. It is put into a glazed porcelain crucible, which is kept at a temperature of about 392° F. by a little charcoal. The negative electrode is a plate of platinum, upon which the aluminium is deposited, mixed with chloride of sodium, in the form of a grayish crust. The positive electrode consists of a perfectly dry porous vessel, containing some fused chloride of aluminium and sodium, into which a cylinder of charcoal*, conducting the electricity, is immersed. To this is conveyed the chlorine and a little chloride of aluminium, arising from the decomposition of the double salt. This chloride would be volatilized and lost if no chloride of sodium were added in the porous vessel. The fixed double chloride is reconstituted, and the vapours cease. A small number of elements (two, in fact, are sufficient) is all that is necessary for the decomposition of the double chloride, which only presents a very weak resistance to electricity.

The plate of platinum is removed when it is sufficiently loaded with the metalliferous deposit. It is allowed to cool, the saline mass is rapidly broken off, and the plate again introduced into the current. The crude substance detached from the electrode is put into a porcelain crucible enclosed in an earthen one, and fused. After cooling, it is treated with water, which dissolves a large quantity of chloride of sodium, and a gray metallic powder is obtained, which is formed into an ingot by several successive fusions, in which the double chloride of aluminium and sodium is employed as a flux.

The first portions of metal obtained by this process are almost always brittle; it is the cast aluminium which has been mentioned. The pile will however give a metal as fine as that produced by sodium, but it is necessary to make use of a purer chloride of aluminium. And, in fact, in this latter process, we get rid, by means of hydrogen, of the silicium, the sulphur, and even the iron, which passes into the state of protochloride at the temperature at which the operation is carried on, whilst all these impurities remain in the liquid, which is decomposed by the pile, and are removed along with the first portions of the reduced metal.—*Comptes Rendus*, August 14, 1854, p. 321.

Presence of Sugar in the Liquid of Ascites. *By* Dr. Frerichs.

The author relates a case of fatty liver in a girl, aged nine. The hepatic disorder was accompanied by considerable ascites, even before there was any indication of hardening of the substance of the

with the oxided minerals, from which they only differ in containing chlorine in place of oxygen.

* The most dense charcoal very quickly dissolves in the bath, forming a powder; hence the necessity of the porous vessel.

organ. The liquid, removed by a trochar in the usual manner from the peritoneal cavity, was rich in sugar, a substance hitherto not found in this situation. The author has often since failed to detect this substance in other similar cases, proceeding from disease both of the liver and the heart. He considers the fact of interest, as illustrating the part which the liver takes in the development of sugar in the human body.—*Wien. Med. Wochenschr.* vi. 1854; *Med. Times*, Aug. 16, 1854.

On the Action of the Halogen Compounds of Æthyle and Amyle on some Vegetable Alkaloids. *By* Mr. Henry How, Assistant to Professor Anderson, Glasgow University.

[Concluded from page 350.]

Action of Chloride of Amyle upon Strychnine.

Chloride of Amylostrychnine.—Strychnine, placed in contact with chloride of amyle, is found to undergo very slowly a change quite analogous to that with iodide of æthyle under the same circumstances. About 80 grs. of the finely powdered alkaloid being sealed up in a strong tube with 2 fluid drms. of chloride of amyle and some 10 of absolute alcohol, the vessel was placed in boiling water, and retained at the same temperature for a long time. Complete solution took place in about fifty hours, and the heat was continued nearly forty-eight hours longer. The rather oily liquid deposited nothing on cooling, and left, on distillation to a syrup, a thick mass, which finally dried up to a crystalline residue. This proved to be the chlorine salt of a base generally analogous to the æthyle product; it was very soluble in hot water, and crystallizable from a very strong boiling solution on cooling, or a more dilute one by evaporation, in fine colourless prisms.

I must mention that, in the first place, the whole of the product was dissolved in hot water, and the fluid evaporated to crystallization; the resulting crystals have their composition represented in analysis I. below, and must have contained any strychnine salt, or a great part of it, had any been originally present, as this is less soluble than the new one.

The entire mother-liquor of these crystals was supersaturated by ammonia; no precipitate appeared for some time; on stirring, however, a certain quantity of a crystalline deposit fell, which presented the characters of strychnine. The ammoniacal fluid was suffered to stand two hours or so, and then filtered and evaporated to dryness at 212°. The residue was found to be completely soluble in hot water, or left but a little insoluble strychnine, and was made to crystallize like the first product. These are the crystals employed in analysis II., and could contain no strychnine.

The identity of the analytical results furnished by these two salts, and the appearance of the strychnine, caused me to make direct experiments with ammonia, to be described presently; in the meantime, the analyses of the salts, obtained as above, are given; the

chlorine was determined in a specimen different from either of the others:—

	I.	II.	III.	Mean.			
Carbon	69·16	69·58	..	69·37	52 = 312		69·41
Hydrogen..	7·80	7·88	..	7·84	34	34	7·56
Nitrogen ..	..	..	..	..	2	28	6·22
Oxygen....	..	..	..	..	5	40	8·92
Chlorine ..	..	..	8·03	8·03	1	35·5	7·89

These numbers indicate a change quite analogous to that before seen to obtain with iodide of æthyle, and it may be expressed thus:—

$$\underbrace{C^{42}H^{22}N^2O^4}_{\text{Strychnine.}} + C^{10}H^{11}Cl = \underbrace{C^{42}H^{22}N^2O^4, C^{10}H^{11}, Cl = C^{52}H^{33}N^2O^4Cl}_{\text{New salt.}};$$

but the salt, as deposited from water, retains an equivalent of the same at 212°, and is, according to the above analysis, $C^{52}H^{33}N^2O^4Cl + HO$; while, in the air-dry state, the crystals contain in addition 7 atoms, 12·54 per cent., which they readily part with; the formula $C^{52}H^{33}N^2O^4Cl, HO + 7Aq$ requires 12·29.

The hydrated chloride of amylostrychnine crystallizes from water in fine, thick, colourless, oblique, rhombic prisms, which have a peculiar greasy appearance when dry; it is very soluble in alcohol. Its aqueous solution is not affected by dilute potash, or by ammonia, except when left long in contact; but is immediately precipitated by strong potash, the salt being thrown down unchanged. Oxide of silver eliminates the chlorine, leaving the base dissolved. When heated, the dry salt fuses, and gives off, first water, then acid vapours, and finally, with intumescence and blackening, alkaline fumes of a very nauseous odour, which also affect the throat most unpleasantly.

Its aqueous solution gives, with that of mercuric chloride, a heavy white precipitate, which is difficultly soluble in boiling water, and is deposited in the cold in very small and separate crystals; these seem, when magnified, to be prisms and octahedra; it furnishes with chloride of gold an insoluble, amorphous, yellow precipitate. With bichloride of platinum, a pale yellow uncrystalline precipitate is obtained, but this could not, in three trials, be obtained of constant composition; the platinum came out always much too high, even above that of the strychnine salt itself, in two cases, by 0·3 to 0·7 per cent.

Bichromate of Amylostrychnine.—This salt was obtained from the mother-liquor of salt II. above, by addition of bichromate of potash; it fell as a crystalline yellow salt, soluble in boiling water; when ignited, 6·418 grs., dried at 212°, gave 0·965 gr. sesquioxide of chromium. The per-centage of anhydrous chromic acid corresponding to this number is 19·63; and 19·37 is that required by a salt analogous to that of the æthyle base, of the formula $C^{52}H^{33}N^2O^4CrO^4, HCrO^4$. There exists also a crystalline chromate.

Nitrate of Amylostrychnine.—This was prepared from the crystals of the chloride I., by double decomposition with nitrate of silver in warm liquids. It is more soluble than the corresponding salt of æthylostrychnine; but it is by no means of great solubility in cold

water, though readily taken up in the heat. It crystallizes from hot water in very beautiful radiated groups of colourless needles; the analysis of these, dried at 212°, gave,—

Carbon.....	65·32	52 =	312	65·54
Hydrogen.....	7·26	34	34	7·14
Nitrogen	..	3	42	8·82
Oxygen.....	..	11	88	18·50

and it appears that this salt is also not anhydrous at 212°, its formula being $C^{52} H^{33} N^2 O^4 NO^6 + HO$.

The air-dried crystals contain in addition 10 atoms of water =15·90 per cent.

The aqueous solution of the nitrate gives, with that of mercurous nitrate, a crystalline deposit in the form of colourless needles; these are, no doubt, a double salt.

Hydrate of Amylostrychnine.—The chloride furnishes, with oxide of silver in water, a rich red-purple fluid of a highly alkaline nature, which agrees most strikingly in its characters with the solution of æthylostrychnine; indeed the two might be readily mistaken for each other; their deportment with metallic salts, and on evaporation, *in vacuo* or at 212°, is precisely the same. The flocky basic product, by evaporation in the case of each, bears possibly the same relation to its congener which the parent bases mutually possess.

The residue left *in vacuo* dissolves to a very rich purple fluid in hot absolute alcohol, and æther causes in this solution an abundant and quickly appearing deposition of radiated white needles. I have not as yet analysed these, but I apprehend they must bear a close analogy to the hydrate of æthylostrychnine.

The chloride of amylostrychnine seeming to have a tendency to decompose in contact with ammonia, some solutions of the salt were supersaturated with this alkali; in no instance did any immediate precipitate occur; but in all, after the lapse of a shorter or longer period, crystalline deposits were formed, while the fluids assumed a reddish-brown colour; in some cases the product was but microscopic at the end of a fortnight, while other specimens furnished within this time quite a decided crystallization on the sides of the vessels. These crystals had the qualitative characters of strychnine; and it is easy to imagine a decomposition taking place in which this alkaloid should be regenerated with the formation of amylamine; thus—

$$C^{52} H^{33} N^2 O^4 Cl + NH^3 = C^{42} H^{22} N^2 O^4 + C^{10} H^{13} N, HCl.$$

I have not as yet been able to verify this equation; for there has remained much of the amylostrychnine undecomposed in those cases where I tried to prove the existence of amylamine.

In the hope of hastening the decomposition, some of the mother-liquor of the chloride was sealed in a tube with strong ammonia; the vessel was kept in boiling water for many days; a rather dark-coloured deposit gradually formed, while the liquid itself became brown and rather mucilaginous. At the end of a week the tube was

opened, but I could gain nothing decisive as to the evident decomposition which had taken place, and which seems of a more complex nature than had been anticipated.

The brown deposit was for the most part soluble in hydrochloric acid, but did not present the characters of pure strychnine when reprecipitated by ammonia. Its mother-liquor, from the tube, was evaporated to dryness at 212° to expel the excess of ammonia, and it left a residue which had a most remarkable resemblance to common glue in appearance and odour: this contained the chlorine salt of some base, and when dissolved in water, and decomposed by nitrate of silver in excess, the fluid filtered from the chloride of silver gave in a few minutes a brilliant metallic mirror, but no crystalline salt.

These decompositions, at both temperatures, seem worthy of study. I may mention that chloride of æthylostrychnine, in contact with aqueous ammonia in the cold, also yields, after the lapse of some days, a small deposit of most minute crystals.

I have not at present experimented further with these substances, but hope to be able to render their history more complete, and if possible to clear up some points touched upon in this paper, by studying their especial products of decomposition in these cases. I have the intention also of submitting some of the other alkaloids, yet unexamined, to a similar investigation.

With regard to what has been actually brought forward in the present communication, I would draw the following inferences:—

That the new basic products, æthylo- and amylostrychnine, are analogous to the compound ammonium bases of Hofmann, and quite distinct from the natural fixed alkaloids. In their resemblance to metallic oxides, and the combinations they form with water and acids, they show, in common with these, general family features, while special distinctions exist as individual characteristics, and are to be paralleled in many saline compounds.

That the already complex molecule in the vegetable alkaloids is rendered more susceptible of change by association with additional hydrocarbons.

That, as regards the constitution of strychnine, this alkaloid appears to be made up of a complicated molecule, in which the 1 atom of nitrogen, as in ammonia, &c., is associated with a nitrogenous aggregate of elements, whose function is that of 3 atoms of hydrogen, and whose nitrogen is in a distinct form of combination, as yet undetermined, from that of the first generic atom. The expression of such a composition may be attempted thus:—

$$\underbrace{C^{42}H^{22}N^{2}O^{4}}_{\text{Strychnine.}} = \left\{ C^{42}H^{22}NO^{4} = \left\{ \begin{matrix} H \\ H \\ H \end{matrix} \right\} + N \right\}.$$

And the association of this molecule with any alcohol hydrocarbon occasions the production of an ammonium congener, which, as it

exists in combination with some electro-negative element, may be written thus:—

$$\left\{ C^{42} H^{22} NO^4 = \left\{ \begin{matrix} H \\ H \\ H \\ C^n H^{(n+1)} \end{matrix} \right\} + N + X \right\}.$$

In conclusion, I give a tabular view of the new compounds mentioned in the preceding pages; and, in doing so, I have adopted the termination "ium" for the bases, in analogy with the name ammonium; strychnia, the old name of the alkaloid in English, being, it seems to me, the more appropriate designation for the analogue of ammonia; and it would be but consistent with the ammonium theory, to look upon the alkaloid in entering into combination, with hydrochloric acid for instance, as undergoing the same process as the volatile type, and to speak of the new salt as chloride of strychnium. The products of this investigation, then, are the following:—

Hydriodate of papaverine		$C^{40} H^{21} NO^8 HI$.
Iodide of æthylostrychnium ...		$C^{46} H^{27} N^2 O^4 I$.
Hydrated oxide of do.	crystallized,	$C^{46} H^{27} N^2 O^4 O, HO + 3Aq$.
Nitrate of do.	„	$C^{46} H^{27} N^2 O^4 NO^6$.
Bichromate.....	dried at 212°,	$C^{46} H^{27} N^2 O^4 CrO^4, HCrO^4$.
„	crystallized,	$C^{46} H^{27} N^2 O^4 CrO^4, HCrO^4 + 2Aq$.
Bicarbonate	dry,	$C^{46} H^{27} N^2 O^4 CO^3, HCO^3$.
Platinum compound	crystallized,	$C^{46} H^{27} N^2 O^4 Cl, PtCl^2$.
Chloride of amylostrychnium...	dried at 212°,	$C^{52} H^{33} N^2 O^4 Cl, HO$.
„ „ „	crystallized,	$C^{52} H^{33} N^2 O^4 Cl, HO + 7Aq$.
Nitrate of oxide	dried at 212°,	$C^{52} H^{33} N^2 O^4 NO^6, HO$.
„ „ „	crystallized,	$C^{52} H^{33} N^2 O^4 NO^6, HO + 10Aq$.
Bichromate	dried at 212°,	$C^{52} H^{33} N^2 O^4 CrO^4, HCrO^4$.

Transactions of the Royal Society of Edinburgh, vol. xxi. part 1.

On the Occurrence of Tannic Acids in Woody Plants, and their connexion with the Formation of Wood. By Prof. Pettenkofer.

Some years since, Pettenkofer stated that wood-vinegar contained pyrogallic acid. Further investigations have shown, that the pyrogenous acid contained in wood-vinegar does not behave exactly like pyrogallic acid. Pettenkofer has now found the means of isolating the acid from the wood-vinegar.

The residue of the distillation of wood-vinegar is treated with a concentrated solution of chloride of sodium or of some other salt. The pyrogenous acid dissolves in this, whilst the intermixed resinous matters remain. The acid is then extracted by æther, which leaves it almost in a pure state on evaporation.

This acid is obtained not only by the dry distillation of bark, but also by that of wood; and the quantity of acid is not diminished even when the wood, before distillation, is very finely divided and treated with the usual solvents, even solution of potash.

Hence the author concludes, that this acid is produced from one of the insoluble matters of the wood, from some substance which no doubt stands in near relation to the tannic acids, and which is perhaps produced from this in the course of vegetation, or, on the contrary, may furnish the material for its formation.

Starch and cellulose are not the sources of this pyrogenous acid, for straw, paper, and starch do not furnish it on distillation. It appears therefore that one of the substances incrusting wood furnishes the material for this pyrogenous acid.

A more extended investigation of the distribution of the tannic acids in the vegetable kingdom, which is not yet completed, has already led the author to the result that the tannic acids exist in perennial, but not in other plants, which certainly indicates a close connexion with the formation of wood. *Potentilla tormentilla* and *Solanum Dulcamara*, which are perennial plants, contain tannin; the annual species, *Potentilla anserina* and *Solanum tuberosum*, contain none.—Buchner's *Neues Repertorium*, iii. p. 74.

On the Composition of Tannic Acid. *By* A. Strecker.

It appears from my experiments, that tannic acid and the tannins in general are much more complex bodies than is generally supposed. In fact, by the action of mineral acids, of alkalies, or of ferments, they are resolved into glucose and a new acid by fixing the elements of water. This resolution, which I announced two years ago, has served me as a starting-point in the determination of the molecule of tannic acid.

According to the analyses of Pelouze, Liebig and Berzelius, the molecule of tannic acid is expressed by the formula $C^{18}H^{8}O^{12}$, and it is supposed that in its neutral salts 3 equivs. of water of this formula are replaced by 3 equivs. of metallic oxide. There is nevertheless only one tannate (that of lead) which appears from analysis to contain the carbon and metal in the proportion of 18 : 3 equivs.

Perceiving from the splitting of tannic acid into glucose ($C^{12}H^{12}O^{12}$) and gallic acid ($C^{14}H^{6}O^{11}$) that the above formula could not express the molecule of acid, I undertook a series of experiments to determine the true formula of tannic acid; of these I now lay the results before the Academy.

To obtain tannic acid in a pure state, I purified the acid prepared by the method of M. Pelouze, in two ways; one portion was dissolved in pure æther and the solution precipitated by water, the other portion was dissolved in water and precipitated by æther. Under these conditions two or three distinct strata are obtained, of which the heaviest consists of tannic acid, dissolved in the ætherial fluid. This syrupous liquid was dissolved in water and then evaporated *in vacuo*; the residue was analysed after being dried at 248° F. Ten analyses made with oxide of copper in a current of oxygen gas upon substances obtained at seven different preparations, gave results leading to the formula $C^{54}H^{22}O^{34}$.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	Calculated.
C	52·5	52·2	52·2	52·2	52·2	52·3	52·1	52·2	52·3	52·3	54 = 52·4
H	3·8	3·8	3·7	3·7	3·6	3·9	3·8	3·6	3·7	3·5	22 = 3·6
O	...	...	...	...	...	...	...	...	...	...	34 = 44·0

According to this formula, the resolution of tannic acid into gallic acid and glucose may be represented by the following equation:—

$$C^{54}H^{22}O^{34} + 8HO = 3(C^{14}H^{6}O^{10}) + C^{12}H^{14}O^{14}.$$

This equation is confirmed by the quantities of the two compounds obtained by the decomposition of tannic acid. The former was found to be 87 per cent. (maximum) by Wetherill; of glucose I have obtained as much as 22 per cent.

The quantity of water which may be displaced by metallic oxide in the molecule $C^{54}H^{22}O^{34}$ I have determined directly by digesting tannic acid with oxide of lead, and the analysis of the neutral and basic salts. By the former method I found that the acid loses 4·4 per cent., or 3 equivs. of water, which is confirmed by the analysis of the salts of lead prepared by precipitation, in which the composition of the anhydrous acid is represented by the formula $C^{54}H^{19}O^{31}$, differing by 3 equivs, of water from the formula $C^{54}H^{22}O^{34}$. The precipitates obtained by tannic acid and acetate of lead contain from 3 to 10 equivs. of oxide of lead, in proportion to C^{54}. The analyses of tannates made by Pelouze, Liebig, Berzelius, Mulder and Büchner, agree with the new formula of tannic acid, if we suppose that some salts do not lose all their water at 212° F., or that they were not completely dried.

According to Berzelius, tannic acid combines with sulphuric or muriatic acid, when these acids are added to a solution of tannic acid in water. In these cases precipitates are obtained which are dissolved at the commencement, until the fluid contains an excess of sulphuric or muriatic acid. These compounds are distinguished from the conjugate acids, as the mineral acid can be separated therefrom by salts of baryta or silver. The analysis of these precipitates shows that they are nothing but tannic acid imbued with the acid liquor in which they are deposited. In fact, this sulphuric tannin only contains from 2 to 4 per cent. of sulphuric acid; and the muriatic tannin, when placed *in vacuo* over quicksilver, loses its muriatic acid completely. Moreover, these precipitates differ in no respects from tannic acid, which has been acidulated with a mineral acid. The formation of a precipitate by a mineral acid in a solution of tannin is therefore perfectly conformable to the precipitation of the same solution by chloride of sodium and other alkaline salts, and even by æther, and must be explained by a diminution of the solubility of the tannin in consequence of the change in the solvent.

Gallic acid, which, according to some chemists, contains in the formula $C^{11}H^{6}O^{10}$ 4 or 2 equivs. of water, is, from my analyses, a tribasic acid; and the yellow lead salt, regarded by Liebig and Büchner as a neutral salt, and represented by the formula

$$4PbO . C^{14}H^{2}O^{6},$$

is a basic salt, which, when dried at 248° F., has a composition represented by the formula

$$4PbO . C^{14} H^{3} O^{7}, \text{ or } 3PbO . C^{14} H^{3} O^{7} + PbO.$$

In fact, five analyses performed with materials prepared at different times gave 75·9 to 76·1 per cent. PbO; numbers which approach much more closely to the latter formula than to that of Liebig and Büchner.—*Comptes Rendus*, July 3, 1854, p. 49.

On the Composition and Properties of Fats. *By* D. Heintz.

According to the investigations of Heintz upon fats, these bodies always furnish, on saponification with potash, fatty acids and glycerine, as indeed has been known ever since Chevreul's experiments. According to the author's experiments, the acids of the acetic acid series, expressible by the formula $C^{n} H^{n} O^{4}$, occur together with oleic acid in fats; but those acids of this series in which n is a number not divisible by 4, are absent from the products of the saponification of fats. Thus the non-existence of margaric acid ($C^{34} H^{34} O^{4}$) as a chemically pure substance is particularly proved.

In his most recent investigation, Heintz shows that even the saponification of spermaceti furnishes no other fatty acids than those which can be expressed by the general formula $C^{4n} H^{4n} O^{4}$ (n=a whole number). The cetic acid ($C^{30} H^{30} O^{4}$) and cocic acid ($C^{26} H^{26} O^{4}$), formerly supposed by him to exist in that substance, are mixtures of at least two of the fatty acids of spermaceti. Besides stearic acid ($C^{36} H^{36} O^{4}$) and palmitic acid ($C^{32} H^{32} O^{4}$), the occurrence of which in spermaceti has already been proved by the author, two other acids have also been obtained in a chemically pure state from that substance. These are myristic acid ($C^{28} H^{28} O^{4}$) and laurostearic acid ($C^{24} H^{24} O^{4}$). Their separation was effected by the method of partial precipitation combined with that of recrystallization.

Myristic acid in the pure state has hitherto been unknown, for Playfair, who first mentioned it, gives its melting-point at 120° F., whilst it really fuses at 129° F. When cold, it is exactly like palmitic acid, appearing in scaly crystals. It is however more readily soluble in alcohol, and crystallizes from this solution in laminæ of a pearly lustre. Analyses of the acid itself, as well as of its silver, lead, copper, baryta and magnesia salts, furnish concordant results leading to the formula $C^{28} H^{27} O^{3} + RO$. Its combination with oxide of æthyle (myristic æther) melts at 83°·3 F., crystallizes very beautifully in the cold, and dissolves readily in hot alcohol. Its composition is $C^{28} H^{27} O^{3} + C^{4} H^{5} O$.

Laurostearic acid, which was prepared by Marsson from the oil of laurel berries, by Sthamer from the fat of pichurine beans, and by Görgey from cocoa-nut oil, melts with rather more difficulty than stated by these chemists. Its melting-point is 110°·5 F. It dissolves very readily in alcohol, and only crystallizes partially from this solution at a low temperature. It is transparent, but still forms scaly crystals; it consists of $C^{24} H^{23} O^{3} + HO$, as appears from analyses

not only of the acid itself, but also of its silver, lead and baryta salts.

Gottlieb has already noticed, that stearic acid mixed with margaric acid in certain proportions, may acquire a lower melting-point than that of the last-mentioned acid. As this, according to the author's previous investigations, is a mixture of stearic and palmitic acids, this peculiarity must be a property of this mixture, which in fact is the case, as margaric acid itself is nothing but a mixture of palmitic acid with stearic acid, which melts more readily than the former acid. Heintz has found, however, that any two fatty acids may form a mixture possessing a lower melting-point than even the most fusible of them in a pure state. He has drawn up the following tables, showing the melting-point and mode of solidification of mixtures in simple proportions of every two of the four acids,—stearic acid, palmitic acid, myristic acid, and laurostearic acid:—

A mixture of stearic acid. parts.	palmitic acid. parts.	Melts at	Solidifies at	Form of solidification.
100	0	156·56° F.	.. °F.	scaly crystalline.
90	10	152·96	144·5	the same.
80	20	149·48	140·54	finely acicular.
70	30	145·08	106·68	the same.
60	40	140·48	133·70	uncrystalline tubercular.
50	50	133·88	131·00	laminar crystalline.
40	60	133·40	130·1	the same.
35	65	132·08	129·74	uncrystalline, shining.
32·5	67·5	131·36	129·2	the same.
30	70	131·18	129·2	the same, lustreless.
20	80	135·5	128·84	very indistinctly acicular
10	90	140·18	130·1	beautifully acicular.
0	100	143·6	..	scaly crystalline.

A mixture of palmitic acid. parts.	myristic acid. parts.	Melts at	Solidifies at	Form of solidification.
100	0	143·6°F.	.. °F.	scaly crystalline.
95	5	141·98	136·4	the same.
90	10	140·18	132·26	the same.
80	20	136·4	128·3	fine scaly crystals.
70	30	130·82	124·34	extremely fine needles.
60	40	124·7	121·1	uncrystalline tubercular.
50	50	119·04	113·54	large laminar crystals.
40	60	116·6	110·66	indistinctly laminar.
35	65	115·7	..	uncrystalline opake.
32·5	67·5	115·16	111·2	the same.
30	70	115·16	110·66	the same.
20	80	121·1	106·34	uncrystalline.
10	90	125·54	113·54	in long needles.
0	100	128·84	..	scaly crystals.

A mixture of myristic acid. parts.	laurostearic acid. parts.	Melts at	Solidifies at	Mode of solidification.
100	0	128·84° F.	.. ° F.	scaly crystals.
90	10	125·54	117·14	the same.
80	20	121·28	112·1	fine crystals, neither distinctly scaly nor acicular.
70	30	116·06	102·2	the same.
60	40	109·4	102·2	uncrystalline, with a few shining spots.
50	50	99·32	96·26	large laminar crystals.
40	60	98·06	92·3	uncrystalline, with a few shining spots.
30	70	95·18	90·14	uncrystalline.
20	80	101·3	91·4	the same.
10	90	106·34	96·8	acicular crystals.
0	100	110·48	..	scaly crystals.

A mixture of stearic acid. parts.	myristic acid. parts.	Melts at	Form of solidification.
0	100	128·84° F.	
10	90	125·06	uncrystalline opake.
20	80	119·04	indistinctly crystalline.
30	70	118·76	laminar crystals.
40	60	122·72	beautiful large laminar crystals.

A mixture of palmitic acid. parts.	laurostearic acid. parts.	Melts at	Form of solidification.
0	100	110·48° F.	
10	90	106·7	uncrystalline.
20	80	98·78	indistinctly crystalline.
30	70	100·94	small laminar crystals.
40	60	104·18	beautiful large laminar crystals.

A mixture of stearic acid. parts.	laurostearic acid. parts.	Melts at ° F.	Form of solidification.
0	100	110·48° F.	
10	90	106·7	uncrystalline.
20	80	101·3	uncrystalline, warty.
30	70	110·12	the shining faces of small crystals appearing on the surface.
40	60	123·44	uncrystalline, warty.

From these tables it appears that,—

1. By the addition of any fatty acid to from 4 to 10 times its

quantity of another fatty acid, the melting-point of the latter is lowered, even though the acid added be more difficult of fusion.

2. The mixture of two acids differing by $C^4 H^4$, which possesses the lowest melting-point, consists of about 3 parts of that which contains the most carbon and 7 parts of the other.

3. The mixture of two acids differing by $C^8 H^8$, which possesses the lowest melting-point, consists of about 25 parts of the richest in carbon and 75 of the other.

4. The mixture of two acids differing by $C^{12} H^{12}$, which possesses the lowest possible melting-point, consists of about 20 parts of that which contains most carbon and 80 of the other.

5. Thus the greater the difference in the amount of carbon in two acids, the smaller is the quantity of that which contains most carbon required to produce the lowest melting-point.

6. The greater the amount of carbon in two acids differing by $C^4 H^4$, the less is the difference between the melting-point of the pure acids and the lowest point of the mixed acids.

7. If to 9 parts of an acid $C^{4n} H^{4n} O^4$, we add 1 part of an acid $C^{4(n+1)} H^{4(n+1)} O^4$, and to a similar quantity of the former also 1 part of an acid $C^{4(n-1)} H^{4(n-1)} O^4$, two mixtures are obtained possessing the same melting-point. The same applies, or nearly so, to mixtures of 8 and 7 parts $C^{4n} H^{4n} O^4$, and 2 and 3 parts $C^{4(n+1)} H^{4(n+1)} O^4$, or $C^{4(n-1)} H^{4(n-1)} O^4$.

8. A mixture of a little more than 3 parts of the acid $C^{4n} H^{4n} O^4$ with a little less than 7 parts of the acid $C^{4(n+1)} H^{4(n+1)} O^4$, possesses the same melting-point as the acid $C^{4n} H^{4n} O^4$ in the pure state.

The mixture of 9 parts $C^{4n} H^{4n} O^4$ with 1 part $C^{4(n+1)} H^{4(n+1)} O^4$, solidifies in acicular crystals (like margaric acid).

10. The mixture of equal portions of fatty acids differing by $C^4 H^4$, solidifies in large laminar crystals (like anthropic acid).

11. Mixtures of 20 to 30 parts $C^{4n} H^{4n} O^4$ with 80 to 70 parts $C^{4(n+1)} H^{4(n+1)} O^4$, crystallize in extremely fine needles.

12. Mixtures of 60 parts $C^{4n} H^{4n} O^4$ with 40 parts $C^{4(n+2)} H^{4(n+2)} O^4$, solidify in large laminar crystals (like anthropic acid).

Heintz has also found that when, to a mixture of two acids differing by $C^4 H^4$, a small quantity of one containing a larger amount of carbon, and consequently more difficult of fusion, is added, the melting-point becomes still lower by several degrees. For instance, if about 3 to 4 parts of stearic acid, which melts at 124°·26 F., be added to the mixture, fusing at 115°·16 F., of palmitic acid (which fuses at 143°·6 F.) and myristic acid (which melts at 128°·84 F.), the mixture obtained fuses at 110°·84 F. Such mixtures of these fatty acids consequently behave very like the readily fusible metallic mixtures, which also consist of three metals (lead, tin and bismuth). —*Bericht der Akad. der Wiss. zu Berlin*, 1854, p. 207.

On some Combinations of Hydrargyromethyle and Hydrargyræthyle. *By* A. Strecker.

Frankland found a short time since, that when iodide of methyle and iodide of amyle in contact with mercury are exposed to the

influence of the solar rays, crystals are formed of which the composition is expressed by the formulæ $C^2 H^3 Hg^2 I$ and $C^{10} H^{11} Hg^2 I$, and to which he gave the names of iodide of hydrargyromethyle and iodide of hydrargyramyle. He did not succeed in producing an analogous compound with iodide of æthyle, although the existence of this combination might be presumed.

Before I was acquainted with Frankland's experiments, I had already obtained the iodide of hydrargyræthyle, which may easily be produced from a mixture of iodide of æthyle and mercury under the influence of diffused light. After some time crystals are formed, of which the quantity increases until the whole of the liquid sets into a mass. The crystals dissolve in boiling æther and alcohol, from which they separate in thin, colourless, shining laminæ. They sublime at 212° F., but only fuse at a higher temperature. They do not dissolve in water, but are soluble in ammonia and in solution of potash, from which they crystallize again without decomposition. On analysis I found their composition to be $C^4 H^5 Hg^2 I$. With nitrate of silver they furnish iodide of silver and nitrate of hydrargyræthyle, $C^4 H^5 Hg^2 O . NO^5$, which crystallizes on evaporation in colourless prisms. Chloride of sodium precipitates chloride of hydrargyræthyle, $C^4 H^5 Hg^2 Cl$, from the watery solution of the nitrate; it cannot be distinguished from the iodide by its characters. These æthyle compounds are decomposed by sun-light, and this is the reason why Mr. Frankland did not obtain them. I have also prepared the nitrate of hydrargyromethyle; its composition is $C^2 H^3 Hg^2 O . NO^5 + HO$. —*Comptes Rendus*, July 3, 1854, p. 57.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 15, 1854. (The Earl of Rosse, President, in the Chair.)

"On the Constitution of Coal-tar Creosote," by Prof. Williamson.

For some years past it has been a debated question among chemists, whether the peculiar body originally described by Reichenbach as creosote, and subsequently analysed by Ettling and others, has any real existence, or whether the properties which were attributed to it are not to be more correctly ascribed to the hydrate of phenyle, which can be obtained in a state of great purity from at least one sort of commercial creosote by mere distillation, and which possesses in an eminent degree the antiseptic properties for which creosote is remarkable.

With a view of obtaining some light on this question, Mr. Fairlie undertook, in the laboratory of University College, an investigation of the portions of coal-tar creosote which boil higher than the hydrate

of phenyle. The result of his experiments has been to show that a body homologous to hydrate of phenyle may be obtained from the crude creosote, in fact the next term of the series above hydrate of phenyle itself. Some qualities of commercial creosote contain a greater quantity of this *hydrate of cresyle* (as it may be termed) than others; and it is most advantageously prepared from those portions which in the first distillation come over between 200° Cent. and 220°. After a great number of fractional distillations, a colourless, highly dispersive liquid is obtained, boiling at 203° Cent., and possessing the composition represented by the formula $C^{14}H^8O^2$.

This hydrate of cresyle resembles the corresponding phenyle compound in most of its properties; but it may be easily distinguished from that compound by its almost complete insolubility in aqueous ammonia.

When gradually mixed with sulphuric acid, it becomes of a beautiful rose-colour, and gives rise to sulpho-cresylic acid.

The action of nitric acid upon hydrate of cresyle is very violent, and almost explosive if the acid is used in a concentrated state and at so high a temperature as the common atmospheric; even very dilute nitric acid transforms the compound into a brown tarry mass from which no definite substance can be extracted. By cooling some nitric acid in a frigorific mixture and allowing some similarly cooled hydrate to fall into it drop by drop and with constant agitation, a red-coloured solution was obtained, which by dilution with water and subsequent neutralization by potash yielded a crop of short needle-shaped crystals of an orange-red colour, and possessing a greater solubility in water than the salt of carbazotic acid. This salt was found by analysis to possess the composition of a homologue of carbazotate of potash; so that it is the potash salt of a hydrate of cresyle in which three atoms of hydrogen are replaced by hyponitric acid,

$$C^{14}\begin{matrix} H^4 \\ (NO^4)^3 \end{matrix} O, KO.$$

The same acid was obtained by the action of nitric acid upon an alcoholic solution of the hydrate containing urea; but in attempting to repeat this experiment on a larger scale the mixture became hot, and the whole of the substance was destroyed with almost explosive violence.

When treated with pentachloride of phosphorus this hydrate of cresyle is decomposed in like manner with the hydrate of phenyle, as described by Mr. Scrugham, yielding a chloride of cresyle and a phosphate of the same radical.

By the action of this phosphate in an alcoholic solution of acetate of potash, a peculiar oleaginous body is obtained possessing an odour entirely different from that of the hydrate, and decomposable by potash with production of acetate and cresylate.

A similar reaction ensues when the phosphate is distilled with æthylate of potash, and a cresylate of æthyle is thus obtained.

In the numerous distillations which were performed for the purification of the hydrate of cresyle, some circumstances were observed which led to a suspicion that the body undergoes a change of composition, either through the distillation itself, or by some influences accompanying it. These circumstances were,—1st. A tarry residue, from a liquid which when introduced into the retort was perfectly colourless. 2nd. The formation of a small quantity of water in the commencement of such a distillation, though none was contained in the substance used. 3rd. The gradual lowering of the boiling-point of the whole liquid by a great number of distillations. These facts, taken in conjunction, naturally suggested that the oxygen of the air contained in the retort might act upon the substance, and thus gradually reduce it to hydrate of phenyle.

In order to test the correctness of this hypothesis, the atmospheric air was expelled from the distilling apparatus by dry hydrogen gas, and the distillation performed in a pure atmosphere of this gas. A great number of distillations performed in this manner were at exactly the same temperature, and all the other anomalies were simultaneously removed. It was however found that the liquid always boiled at a lower temperature in hydrogen than in atmospheric air, the difference being about 2° Cent., and this without any alteration of the pressure on the surface of the boiling liquid. A similar fact was noticed in the distillation of hydrate of phenyle, and also of some other liquids.

"On the Immediate Principles of the Excrements of Man and Animals in the Healthy Condition," by William Marcet, M.D.

The author describes a new method of extracting the immediate chemical constituents of the excrements of Man and animals, and gives an account of the substances obtained by its employment.

Healthy human fæces are boiled to exhaustion in alcohol. The residue is insoluble in æther, and yields to boiling water nothing but ammoniaco-magnesian phosphate. The strained alcoholic solution deposits, on standing, a sediment, from which it is decanted and then mixed with milk of lime. The subsiding lime is of a yellow-brown colour; it is dried on filtering-paper and treated with æther, cold or hot, and the solution thus obtained yields, on spontaneous evaporation, beautiful silky crystals, which are purified by solution in a mixture of alcohol and æther, repeated filtration through animal charcoal and recrystallization; they then appear in circular groups, have the form of acicular four-sided prisms, and polarize light very readily. This crystalline body the author proposes to call *Excretine*. It is very soluble in æther, cold or hot, but sparingly soluble in cold alcohol; its solution has a decided though weak alkaline reaction. It is insoluble in hot or cold water, and is not decomposed by dilute mineral acids. It fuses between 95° and 96° C., and at a higher temperature burns away without inorganic residue. When boiled with solution of potash it does not dissolve. As to its qualitative constitution, it is found to contain nitrogen and sulphur, though in

small proportions; the products of its decomposition have not yet been investigated.

The author has in several cases observed the excretine to crystallize directly in the alcoholic solution of fæces before the addition of lime, and has scarcely any doubt that it exists for the most part in a free state in the excrements, and constitutes one of their immediate principles. As to its source, he observes that it appeared in excess when a considerable quantity of beef had been taken, and in less than the usual quantity in a case of diarrhœa attended with loss of appetite; but none could be directly obtained from beef on subjecting it to the same process of extraction as fæces. Neither could it be found in ox-bile, the urine, or the substance of the spleen. From the difficulty of obtaining the contents of the human small intestine in a healthy state, its presence or absence in that part of the alimentary canal has not yet been satisfactorily determined.

The lime precipitate, after having been thus thoroughly deprived of the excretine by æther, is next treated with hydrochloric acid, and water or alcohol, by which means margaric acid is extracted from it. The author is uncertain whether the margaric acid of the fæces is free or combined with excretine, but he is disposed to conclude that the neutral fats are decomposed in the intestinal canal and their acid set free. Not having been able to detect stearic acid in human evacuations, he supposes that what is contained in the fat of mutton or beef taken as food must be converted into margaric acid in its passage through the alimentary canal.

The lime precipitate, freed from excretine and dissolved in alcohol by means of hydrochloric acid, forms a dark port-wine-coloured solution, from which the margaric acid is deposited. On then adding water to the solution and concentrating it on the water-bath, a flaky colouring matter separates, which, being purified by solution in æther and washing with water, is obtained as a dark-brown or black amorphous substance, similar to the colouring matter of blood, and to that which Dr. Harley has lately extracted from urine.

The matters brought down with the lime having been thus extracted, the sediment which spontaneously subsides from the alcoholic solution of fæces before its treatment with the milk of lime, is next examined. This deposit appears to be complex in its nature; it has a strongly acid reaction, and presents under the microscope small oily globules, mixed sometimes with crystals of excretine and accompanied by a yellow amorphous matter. By boiling with alcohol and filtration, a residue remains which the author has not yet examined, and two substances are obtained from the filtrate. The first is deposited on cooling; when collected and dried on filtering-paper it has a granular character and is quite colourless; it is very sparingly soluble in æther, fuses by heat, and burns with a bright fuliginous flame, leaving a white residue consisting of phosphate of potash. The author has not yet been able satisfactorily to decide whether this is a pure immediate principle or not; he is inclined to consider it as a combination of phosphate of potash and a pure organic sub-

stance. The filtered fluid, after separation of this matter, still contains a substance which he has called *Excretolic acid*. It is obtained by evaporating to dryness, extracting the residue with æther, adding to the æthereal solution alcohol and lime-water, and heating. The acid is precipitated in combination with lime, from which it is separated by means of sulphuric or hydrochloric acid and solution in æther. The æthereal solution, after being well washed with water to remove mineral acid, yields the pure excretolic acid on evaporation. This body is of an olive colour; it fuses between 25° and 26° C., and at a higher temperature burns without residue. It is insoluble in water and in a boiling solution of potash; very soluble in æther, sparingly soluble in cold alcohol, readily so in hot; its solutions having a marked acid reaction. The author is disposed to believe that in excrement it is combined in form of a salt, with excretine or a basic substance closely allied to it, which is obtained in the filtrate from which the excretolic acid is precipitated in combination with lime in the process of its purification.

The author failed to obtain evidence of the presence either of butyric or of lactic acid in the clear alcoholic solution of fæces filtered from the precipitate formed by the milk of lime. From the above investigation, therefore, it appears that healthy human excrements contain:—

1. A new organic substance, possessing an alkaline reaction, which the author names *Excretine*.

2. A fatty acid, having the properties of margaric acid, but not constantly present.

3. A colouring matter, similar to that of blood and urine.

4. A light granular substance, whose properties have not yet been sufficiently examined to admit of its being considered a pure substance.

5. An acid olive-coloured substance, of a fatty nature, named *Excretolic acid*.

6. No butyric acid and no lactic acid.

The fæces of various animals were submitted to the same process of analysis, with the following results:—

1. The excrements of carnivorous mammalia, viz. the Tiger, Leopard and Dog (fed on meat), contain a substance allied in its nature to excretine, but not identical with it. They contain no excretine; they yield butyric acid, which is not present in human excrements.

2. The excrements of the Crocodile contain cholesterine and no uric acid, whilst those of the Boa yield uric acid and no cholesterine.

3. The fæces of herbivorous animals, viz. the Horse, Sheep, Dog (fed on bread), Wild Boar, Elephant, Deer and Monkey, contain no excretine, no butyric acid and no cholesterine.

THE CHEMICAL GAZETTE.

No. CCLXXXVIII.—October 16, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Contributions towards the Knowledge of Castor-oil.
By J. Stanek.

Bussy and Lecanu first discovered that castor-oil, when distilled without any observable evolution of gas, furnishes a product which at first consists of a volatile, but afterwards of a more fixed oil, but that, after about a third of the oil has passed over, an abundant evolution of a combustible gas, free of carbonic acid, suddenly makes its appearance; whilst the residue, without acquiring colour, is at the same time converted into a bladdery, spongy, elastic mass, which fills the entire vessel in which the distillation is carried on. They also state, that the distillate consists of water, empyreumatic oil, acetic acid, ricinic acid, and elaiodic acid. The residue, when freed from any adherent oil by alcohol, is, according to Bussy and Lecanu, of a pale yellow colour, inodorous and tasteless, and decomposable by heat without fusion; it undergoes but little change by sulphuric, muriatic and nitric acids; is insoluble in water, alcohol or æther, in volatile and fatty oils, or in dilute solution of potash, but is readily saponified by a solution of 1 part of hydrate of potash in 4 parts of water. From the soap, a peculiar thick fluid acid may be separated, which forms a compound with magnesia which is insoluble in alcohol and water.

Unchanged castor-oil, according to Bussy and Lecanu, furnishes by saponification and decomposition of the soap by means of muriatic acid, a mixture of margaritic, elaiodic and ricinic acids.

Saalmüller*, in an investigation of castor-oil carried on in Will's laboratory, found that it furnishes on saponification glycerine, a solid fatty acid and a fluid one; the latter he called ricinoleic acid. Glycerine had already been prepared from castor-oil by Professor Rochleder, by treating its alcoholic solution with muriatic acid gas. In the analysis of the solid fatty acid of castor-oil, Saalmüller obtained no constant results; on one occasion he arrived at numbers agreeing with the composition of stearic acid; on another, numbers corresponding with the formula of palmitic acid. In opposition to the statements of Bussy and Lecanu, Saalmüller showed that castor-oil contains only one fluid fatty acid, for which he gives the formula $C^{38}\,H^{36}\,O^6 = C^{38}\,H^{35}\,O^5 + HO$.

Jules Bouis†, on the contrary, gives the formula $C^{36}\,H^{34}\,O^6$ as the

* Chem. Gaz., vol. vi. p. 74. † *Ibid.*, vol. ix. p. 366.

expression of the composition of this acid, which he calls ricinolic acid, and describes an amide of this acid with the composition $C^{36} H^{35} NO^4$. This amide, as well as the acid, splits on fusion with hydrate of potash into caprylic alcohol and sebacic acid, in accordance with the following equation:—$C^{36} H^{34} O^6$ (ricinolic acid) $+2(KO, HO)=C^{20} H^{16} O^6$, 2KO, sebate of potash $+C^{16} H^{18} O^2$, caprylic alcohol $+2H$. These statements of Bouis were confirmed by Moschnin in Will's laboratory.

In a second paper upon castor-oil (in 1846), Bussy has shown that the product of the dry distillation of castor-oil is a mixture of several products. He took the oily layer which floated upon a watery distillate, and distilled it with water. Ricinic and elaiodic acids remained, whilst acroleine and œnanthole distilled over, contaminated by small quantities of fatty acids which they carried with them. For œnanthole Bussy obtained the formula $C^{14} H^{14} O^2$, and discovered a crystalline hydrate of this body $=C^{14} H^{14} O^2+HO$. He found that nitric acid at 32° F. converted œnanthole into the isomerous crystallized substance metœnanthole. By the action of nitric acid upon œnanthole at a higher temperature, Bussy obtained an oil very similar to (and perhaps identical with) hydruret of cinnamyle, with simultaneous formation of three fatty acids, of which one was œnanthylic acid, which had previously been prepared by Tilley by the action of nitric acid upon castor-oil with heat, and by Arzbächer by the treatment of this oil with sulphuric acid and chromate of potash.

Bussy placed œnanthole in the series of aldehydes, and characterized it as the aldehyde of œnanthylic acid.

Williamson (in 1847) confirmed Bussy's formula for œnanthole. He found that œnanthole, when heated with potash, is resolved into œnanthylic acid, which combines with the potash and a volatile product, which in Williamson's opinion must stand in the same relation to œnanthylic acid as æther to acetic acid. Tilley (in 1848) further examined œnanthole, to which he gave the superfluous name of œnanthal, and found that it is converted by fusing potash into œnanthylic acid, but by the action of potash in the cold into œnanthylic acid and hydruret of œnanthyle. $3(C^{14} H^{14} O^2)$ œnanthole $=C^{14} H^{14} O^4$, œnanthylic acid $+2(C^{14} H^{14} O)$, hydruret of œnanthyle. He also found that œnanthole combines with bisulphite of ammonia to form a crystalline compound. It consequently behaves like all aldehydes, according to the recent researches of Bertagnini.

As the spongy elastic residue of the dry distillation of castor-oil has not hitherto been investigated by any one, the author, by Prof. Rochleder's recommendation, undertook its examination in his laboratory.

To prepare this body, castor-oil was distilled in a glass retort over the open fire. As the residue bubbled up during evolution of gas, the retort was removed from the fire and closed. After cooling, alcohol was poured upon the substance, and this was then taken from the retort. It was pressed between fine linen, allowed to swell up again in alcohol, and again expressed, and by the repetition of

this process deprived of everything that was soluble in alcohol. The same process was afterwards several times repeated with æther, and finally again with alcohol. When dried at 212° F., this caoutchouc-like substance gave the following numbers on analysis:—

Carbon.....	77·11	77·20	42 =	252	77·30
Hydrogen	10·77	10·77	34	34	10·42
Oxygen	12·12	12·02	5	40	12·28

When this mass, which possesses all the properties ascribed to it by Bussy and Lecanu, is saponified with potash, a brown clear solution of soap is produced, whilst an unpleasant but somewhat cinnamon-like odour is evolved. The soap was separated by chloride of sodium. No glycerine could be found in the yellow mother-liquor containing the chloride of sodium, but instead of it there was a small quantity of a greasy brown resin.

The soap was dissolved in water, and solution of chloride of calcium added to it; the lime-soap was dried and treated with æther, which extracted traces of an oleaginous matter. The acid separated from the lime-soap by means of muriatic acid was dissolved in water containing potash, and precipitated by solution of sugar of lead. The lead salt produced in this manner is completely insoluble in alcohol and æther. It was decomposed under alcohol by sulphuretted hydrogen gas, the solution of the acid filtered from the sulphuret of lead, and mixed with water, and the alcohol was then driven off.

When dried at 212° for several hours, the acid formed a thickly fluid, brownish amber-coloured mass, of a peculiar but very faint odour:—

Carbon.....	70·40	36 =	216	70·59
Hydrogen.....	11·00	34	34	11·11
Oxygen.....	18·60	7	56	18·30

By continued drying at 212° F. still more water goes off, but the point could not be attained at which the composition of the substance agreed with the formula $C^{36}H^{31}O^4$, for this acid during drying lost oxygen and hydrogen in the form of water, which could not be contained in it in that condition. After three days' drying at 212° F., the product gave 82·5 per cent. of carbon, agreeing with the formula $C^{36}H^{29}O^3$. Analysis of the lead-salt of the acid:—

Carbon	56·65	36 =	216·000	56·58
Hydrogen	7·66	30	30·000	7·86
Oxygen	7·05	3	24·000	6·29
Oxide of lead.....	28·64	1	111·738	29·27

The acid, both when free and combined with oxide of lead, gave a little less hydrogen than is required by calculation, evidently in consequence of a slight alteration during drying. When a freshly prepared potash soap of this acid is mixed with an excess of soda-lime and exposed to a temperature of 500° F., and the residue supersaturated with dilute sulphuric acid is distilled, a milky distillate of

a penetrating odour is obtained, which when saturated with hydrate of baryta was employed in the formation of a silver salt. 0·262 of this salt, heated to redness, left 0·114 silver, or 46·73 per cent. of oxide of silver. The volatile fatty acid is consequently caprylic acid. No fatty acid was to be recognized in the residue of the distillation of the caprylic acid, which only contained a small quantity of an amorphous resinous mass.

From these experiments the author concludes, that the caoutchouc-like body $C^{42} H^{34} O^5$ is a compound analogous to the fats; when heated, it furnishes like these acroleine; but when saponified, it gives, instead of glycerine, a brown resin, with evolution of an odour like that produced by aldehyde in contact with potash. It is therefore to be supposed that this is not a compound of oxide of glyceryle, but of oxide of acryle.

Its composition, $=C^{42} H^{34} O^5$, may be divided into $C^{36} H^{30} O^3$, pyroricinic acid, $+C^6 H^4 O^2$, acroleine.

The pyroricinic acid, $=C^{42} H^{34} O^7$, obtained by the saponification of the compound, lost 5 equivs. water when kept at 212° F. for a considerable time, and became converted into $C^{36} H^{29} O^2$.

The hydrate of pyroricinic acid, according to the analysis of the lead salt and the caoutchouc-like body, must have a composition agreeing with the formula $C^{36} H^{30} O^3 + HO = C^{36} H^{31} O^4$. It contains 3 equivs. less hydrogen than ricinolic acid, according to Bouis; $C^{36} H^{34} O^6$, ricinolic acid, $-H^3 = C^{36} H^{31} O^4$, pyroricinic acid. If Saalmüller's formula for ricinolic acid were correct, 1 equiv. of hydrogen and 1 equiv. of hydrate of oxide of methyle must be expelled from it, to produce pyroricinic acid.

Whilst ricinolic acid is resolved by hydrate of potash into sebacic acid and caprylic alcohol, taking up 2 equivs. of oxygen, pyroricinic acid under similar circumstances furnishes capric acid. $C^{36} H^{31} O^4$, pyroricinic acid, $+4HO = C^{36} H^{35} O^8$, or $2(C^{16} H^{16} O^4$, capric acid$) + C^4 H^3$. Whether acetic acid is formed during this reaction could not be ascertained with certainty.

It distinctly appears from the experiments, that the production of the volatile products œnanthole, acroleine, &c., stands in no causative connexion with the formation of the caoutchouc-like residue. There are two phases of decomposition, which are successively produced in castor-oil by a high temperature.

In the first the castor-oil is decomposed into acroleine and volatile products of the decomposition of ricinolic acid; the formation of acroleine is accompanied by a formation of water. In the second phase, the caoutchouc-like body and water are produced, with evolution of gas; the formation of water is explained by the conversion of oxide of glyceryle into acroleine, which is contained chemically combined in the solid residue. In accordance with the composition of the solid product, 3 equivs. of hydrogen must be expelled from 1 equiv. of ricinolic acid.

The production of œnanthole from ricinolic acid may perhaps be explained by a simultaneous formation of aldehyde. 2 equivs. of œnanthole and 2 equivs. of aldehyde contain the elements of 2 equivs.

of water and 1 equiv. of ricinolic acid. $C^{36}H^{34}O^{6}$, ricinolic acid, $+2HO=2(C^{14}H^{14}O^{2})+2(C^{4}H^{4}O^{2})$.

Bussy has already stated, that the distillate of castor-oil contains acetic acid, which may very easily be produced from aldehyde by contact with the air. The 2 equivs. of water necessary for the decomposition of the ricinolic acid must be formed when the oxide of glyceryle is converted into acroleine.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xii. p. 588.

On a new Salt of Mercury. *By* E. Sainte-Evre.

In the preparation of cyanide of mercury by means of hydrocyanic acid and oxide of mercury, it is necessary to employ a slight excess of the acid; otherwise the cyanide of mercury dissolves from 2 to 3 equivs. of oxide. But besides this well-known basic salt, another salt may be produced. This is obtained by saturating with oxide of mercury, added in small quantities, a watery hydrocyanic acid, obtained by distilling 10 parts of ferrocyanide of potassium and 7 parts of sulphuric acid, diluted with 14 parts of water, until nearly two-thirds have passed. The mass is then treated with boiling water; this is set by to crystallize, and the cyanide of mercury separated from it. If the mother-liquor be then evaporated until a film of salt appears on the surface, it deposits small mica-like scales.

This new salt has the composition $C^{10}N^{4}Hg^{6}O^{4}$. It is soluble in water; its solution is decomposed by long boiling, depositing metallic mercury. It remains unchanged in diffused light, but acquires colour by the direct action of the sun's rays. When heated, it detonates violently. When heated with sulphuric acid, it evolves carbonic oxide and carbonic acid gases, whilst some metallic mercury is separated, which afterwards gives rise to an appearance of sulphurous acid. At last a magma is left, resembling that furnished by cyanide of mercury under similar circumstances. Analysis:—

Carbon.....	7·73	7·50	10 =	60	8·02
Nitrogen	7·62	7·58	4	56	7·48
Mercury	79·50	79·77	6	600	80·21
Oxygen	..	..	4	32	4·29

As regards the formation of this salt, the atomic proportion above given, $C^{10}N^{4}Hg^{6}O^{4}$, may be reduced to $4(C^{2}NHg)+C^{2}O^{3},Hg^{2}O$. Now as it is known that 1 equiv. of hydrocyanic acid with 4 equivs. of water may become decomposed into ammonia and formic acid, and that formic acid may readily be oxidized into oxalic acid, it is not difficult to explain the formation of the salt; we need only take hydrocyanic acid and oxide of mercury in such proportions that 4 atoms of water may be formed, namely,—

$$4(C^{2}NH)+4HgO=4HO+4(C^{2}NHg);$$

and these 4 equivs. of water in contact with hydrocyanic acid will produce—

$$C^{2}NH+4HO=C^{2}HO^{3},HO+NH^{3}.$$

The formic acid then becomes oxidized at the expense of the oxide of mercury, forming oxalic acid, whilst during the boiling of the fluid ammonia disappears; and in this manner a compound of protoxalate with cyanide of mercury is obtained—

$$C^{10} N^4 Hg^6 O^4 = 4(C^2 NHg) + Hg^2 O, C^2 O^3.$$

Ann. de Chim. et de Phys., xli. p. 461.

On the Behaviour of Iodide of Methyle with Aldehyde-ammonia. *By* M. Saenz Diez.

When iodide of methyle is treated with aldehyde-ammonia in closed tubes, at any temperature up to 212° F., no reaction takes place. But when aldehyde-ammonia is dissolved in alcohol, and an excess of iodide of methyle is added to it, acicular crystals are formed even at ordinary temperatures, whilst the fluid continually becomes darker. The analysis of the crystals led to the formula of hydriodate of trimethylamine—

$$\left.\begin{matrix} C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \end{matrix}\right\} N, HI.$$

Analysis gave:—

Carbon.....	18·627	6 =	36·0	19·24
Hydrogen	5·447	10	10·0	5·34
Nitrogen	7·667	1	14·0	7·48
Iodine	68·269	1	127·1	67·94

Liebig's *Annalen*, xc. p. 301.

On Pyroguaiacine. *By* E. Ebermayer.

The author has obtained a crystallized product by the dry distillation of guaiacum resin. A similar substance has also been described by Deville and Pelletier, from whose analysis the composition of this substance appears to be 76·93 carbon, 7·46 hydrogen, and 15·59 oxygen. It is probably the same substance obtained by Ebermayer, and called by him pyroguaiacine. All specimens of this resin may not produce this body, as Völckel, who has also investigated the products of the distillation of the resin, does not mention it at all, and the author has obtained very different quantities from different resins. In favourable cases he obtained 6 grms. of the pure substance from 6 lbs. of the resin; it was purified by filtration from the oily products, and then by recrystallization from alcohol.

Pyroguaiacine has the constitution $C^{14} H^7 O^2$. It is a neutral body, which may be sublimed without change; it is colourless, but when crystallized from alcohol is of a rose or yellowish colour; it crystallizes in small laminæ or in long needles, swells up in potash, and is extracted again unchanged by alcohol from the air-dried potash compound, after the potash has been saturated with carbonic acid.

When heated for a long time with caustic ammonia, pyroguaiacine acquires a yellow colour; its alcoholic solution, saturated with ammonia, leaves a yellow mass of nearly unchanged pyroguaiacine. When alcoholic solutions of oxide of silver and pyroguaiacine are mixed, silver is reduced.

Dilute sulphuric acid does not act upon pyroguaiacine; but if the latter substance be suspended in water, and concentrated sulphuric acid be dropped into it, and the whole heated, it first of all becomes yellow, then dissolves with a rose-colour, and lastly a blue-black substance separates. Concentrated sulphuric acid becomes very strongly heated in contact with pyroguaiacine; the acid first becomes brown, then dingy green, and lastly deep blue, from the separation of a blue-black body containing sulphur.

Chlorine gas, when passed through water in which pyroguaiacine is suspended, colours this first yellow, and lastly brown. The final product is a brittle readily-pulverizable mass, which, like the wash-water, has a strong musky odour. The analysis I. is of pyroguaiacine crystallized from alcohol; II. is sublimed:—

	I.	II.		
Carbon.....	78·462	78·471	14	78·504
Hydrogen ..	6·901	7·042	7	6·542
Oxygen	14·637	14·487	2	14·953

Journ. für Prakt. Chem., lxii. p. 291.

On the Artificial Production of Taurine. *By* A. Strecker.

The properties of taurine convinced me that we should one day succeed in preparing it artificially. M. Redtenbacher has already attempted to produce taurine by means of aldehyde and bisulphite of ammonia, but he only obtained an isomerous body with different properties. With the same view I undertook the following experiments.

Sulphate of methyle, $C^2H^3O . SO^3$, furnishes with ammonia, sulphomethylane and wood-spirit, according to the formula

$$2(C^2H^3O . SO^3)+NH^3=C^2H^5NS^2O^6+C^2H^4O^2.$$

With sulphate of æthyle we might therefore hope to obtain taurine if the decomposition were analogous,—

$$2(C^4H^5O . SO^3)+NH^3=C^4H^7NS^2O^6+C^4H^6O^2,$$

Sulphate of æthyle. Taurine.

but I found that sulphate of æthyle behaves in a different manner to sulphate of methyle; a conjugate acid is formed, described by me some years ago under the name of sulphæthamic acid.

Substituting methylamine for ammonia, sulphate of methyle might, from analogy, furnish taurine; thus—

$$2(C^2H^3O . SO^3)+C^2H^5M=C^4H^7NO^6S^2+C^2H^4O^2.$$

Sulphate of methyle. Methylamine. Taurine.

I did not try this mode of formation, as I was convinced by expe-

riment that taurine does not give a trace of methylamine on its decomposition with potash.

Nitrite of æthyle, $C^4H^5O . NO^3$, placed by M. Gerhardt amongst the nitryle compounds $\left.\begin{matrix} C^4H^3 \\ NO^4 \end{matrix}\right\}$, would produce taurine (or its isomer) by the action of bisulphite of ammonia, if it behaved like nitro-naphthaline. According to M. Piria, with nitro-naphthaline and bisulphite of ammonia we have—

$$C^{20}H^7NO^4 + 6SO^2 + 2HO = C^{20}H^9NS^2O^6 + 4SO^3.$$
Nitro-naphthaline. Naphthionic acid.

By analogy we should get with nitrous æther,—

$$C^4H^5NO^4 + 6SO^2 + 2HO = C^4H^7NS^2O^6 + 4SO^3.$$
Nitrous æther. Taurine.

Experiment proves that nitrite of æthyle does not act like nitro-naphthaline with bisulphite of ammonia; nitrogen is evolved, and formation of sulphuric and æthylosulphuric acids takes place.

Isæthionic acid, prepared according to M. Regnault, by means of anhydrous sulphuric acid and olefiant gas, when in combination with ammonia only differs from taurine in composition by two equivs. of water,—

$$NH^4O . C^4H^5O . 2SO^3 = C^4H^7NO^6S^2 + HO.$$
Isæthionate of ammonia. Taurine.

This salt fuses at 248° F. without disengaging ammonia, and it might be hoped that at a still higher temperature it would lose water. I first ascertained that taurine might be heated to 464° F. without decomposition or fusion. Isæthionate of ammonia heated to 392° F. began to lose weight; I heated it to 446° F., and kept it at this temperature until it had lost 11 per cent. of its weight. The mass was dissolved in water; on the addition of alcohol it is precipitated in crystals; this precipitate, dissolved in water, furnished by spontaneous evaporation large crystals exactly identical with the crystals of taurine prepared from bile. Like taurine, they bear exposure to a temperature of 464° F. without fusing or acquiring colour; they evolve no ammonia with a solution of potash; they do not precipitate the salts of baryta when boiled with nitric acid or nitro-muriatic acid. When fused with potash and nitrate of potash, they evolve ammonia, and the mass contains sulphuric acid. All these properties being the same as those of taurine, and its mode of formation proving that its composition is similar, this product is identical with the taurine of the bile.—*Comptes Rendus*, July 3, 1854, p. 61.

On the Occurrence of Aconitic Acid in Delphinium consolida. *By* Dr. W. Wicke.

The author has expressed the herb of *Delphinium consolida*; the juice was boiled for half an hour, the lime separated from the strained juice by the addition of oxalate of lime, and acetate of lead added to the fluid. The lead salt was then decomposed by sulphu-

retted hydrogen, the solution, purified by the reproduction of the lead salt and decomposition with sulphuretted hydrogen, evaporated, and the acid extracted from the residue by means of æther. The acid thus obtained is aconitic acid.—Liebig's *Annalen*, xc. p. 98.

On the Action of Alkaline Bisulphites upon Organic Substances. *By* F. Rochleder *and* R. Schwarz.

Amalic Acid, when treated with bisulphite of ammonia, furnishes a substance crystallizing in silky needles, which has the composition $C^{20}\ H^{14}\ N^{4}\ O^{11}$. When exposed, it soon acquires a rose-colour from the ammonia contained in the air; when heated, it evolves a vapour, which is partly colourless and partly purple. It gives no precipitate with chloride of platinum, either in the muriatic acid solution by itself, or after the addition of alcohol and æther. When left a considerable time in contact with a watery solution of chloride of platinum, the substance is decomposed, and a platinum compound, containing both chlorine and nitrogen, separates in beautiful light yellow crystals, which are insoluble in alcohol. They leave a residue of 58·77 per cent. of platinum. (Reiset's compound, $N^{2}\ H^{6}\ PtCl$, requires 58·68 per cent. of platinum.) Analysis gave,—

	I.	II.			
Carbon	43·31	43·16	20 =	120	43·17
Hydrogen	5·41	5·35	14	14	5·04
Nitrogen	20·47	20·07	4	56	20·14
Oxygen	30·81	31·42	11	88	31·65

The *Stearoptene* of oil of Cassia, when boiled with bisulphite of soda, is resolved into a crystalline body, which first separates from the fluid, and a second, which enters into combination with the sulphite of soda. The first is called *benzhydrolic acid* by the authors, the second *benzhydrole*. The stearoptene of cassia-oil must be a compound of these two bodies.

Benzhydrolic Acid separates at first in yellow crystals; by shaking the solution with lime-water, and precipitating the filtered solution by an acid, the acid may be obtained pure and colourless. It forms voluminous snow-white flakes, which may be washed with cold water. The analysis of the acid gave—

Carbon	72·84	42 =	252	73·04
Hydrogen	6·25	21	21	6·09
Oxygen	20·91	9	72	20·87

Benzhydrolate of Silver is obtained by dissolving the acid in lime-water, precipitating a little of the acid by a few drops of very dilute muriatic acid, so that no excess of lime be present, and then adding the solution of nitrate of silver. When heated above 212° F., the salt fuses, and solidifies on cooling in long needles. The analysis of the silver salt gave,—

Carbon	55·14	42	55·07
Hydrogen	4·58	21	4·59
Oxygen	17·50	10	17·46
Oxide of silver	22·78	1	22·85

From the compound of benzhydrole with bisulphite of soda, produced as above stated, when very dilute sulphuric acid is poured over it, a colourless ætherial oil separates, which, after standing for several hours, solidifies in crystals. Both in the form of oil and of crystals, this substance has a strong cinnamon-like odour. It becomes rapidly oxidized when in combination with the sulphite, as well as after its separation. When crystallized from anhydrous alcohol and analysed, it gave,—

Carbon	74·63	42 =	252	74·77
Hydrogen	6·45	21	21	6·23
Oxygen	18·92	8	64	19·00

When the compound of benzhydrole with bisulphite of soda is heated to boiling with water, oil-drops separate on the surface; these collect into an oil resembling cinnamyle, which solidifies on contact with a solid body. By recrystallization from boiling alcohol, pure colourless crystals are obtained, which, when dried in the air, gave on analysis,—

Carbon	75·66	28 =	168	75·6
Hydrogen	6·45	14	14	6·3
Oxygen	17·89	5	40	18·1

When the substance prepared in this manner was heated for several hours to 212° F., by which it was converted into a yellow oil, which solidified on cooling into a crystalline mass, a body was obtained by oxidation possessing nearly the same composition as benzhydrolic acid. Its analysis gave,—

Carbon	72·57	42 =	252	73·04
Hydrogen	6·34	21	21	6·09
Oxygen	21·09	9	72	20·87

The compound of bisulphite of soda with benzhydrole oxidized very readily; but the authors succeeded on one occasion in drying it so rapidly, that it was not altered by oxidation; it then furnished on analysis,—

Carbon	83·92	14 =	84	84·00
Hydrogen	8·39	8	8	8·00
Oxygen	7·69	1	8	8·00

If the formula of the stearoptene, instead of $C^{28} H^{15} O^5$, were we should get,—

$C^{56} H^{29} O^{10} = C^{42} H^{21} O^9$ benzhydrolic acid, $+ C^{14} H^8 O$ benzhydrole.

The product resulting from the action of hydrate of potash upon the oil at a boiling temperature has the composition $C^{42} H^{22} O^{11}$. Its formation depends upon the assimilation of hydrogen and oxygen; thus $C^{42} H^{21} O^9 + HO + O = C^{42} H^{22} O^{11}$.

This stearoptene is also converted by ammonia into a nitrogenized substance. Bisulphite of ammonia converts it into a substance containing nitrogen and sulphur, in which the nitrogen no longer exists as ammonia, nor the sulphur as sulphurous acid.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xii. p. 190.

ANALYTICAL CHEMISTRY.

On the Volumetric Determination of Ferro- and Ferridcyanogen in their Compounds. *By* E. DE HAEN.

THIS method is founded on the simple fact, that a solution of ferrocyanide of potassium, acidulated with muriatic acid, in which therefore free hydroferrocyanic acid is present, is converted, by the addition of permanganate of potash, into the corresponding ferridcyanide. If this transformation be effected in a dilute fluid, containing about 0·2 grm. of ferrocyanide of potassium in 200 to 300 cub. centims., the completion of the reaction is distinctly indicated by the change of the colour of the solution from a pure yellow to a distinct reddish yellow. The determination of ferridcyanogen is effected by the conversion of the ferridcyanide into ferrocyanide by a reducing agent, and then treating the latter with permanganate of potash.

The method requires two fluids of known strength, namely—

1. A solution of pure ferrocyanide of potassium, and
2. A solution of permanganate of potash.

The former is prepared by dissolving 20 grms. of perfectly pure and dry crystallized ferrocyanide of potassium in water, so that the volume of the solution may be exactly 1 litre. Each cubic centimeter will consequently contain 20 milligrms. The second must be so diluted that the contents of a burette must *nearly all* be employed to 10 cub. centims. of the former solution.

To determine first of all the value of the solution of permanganate of potash as compared with that of the ferrocyanide of potassium, 10 cub. centims. of the latter (containing 0·2 grm.) are measured off with a small pipette, diluted with about 250 cub. centims. of water, and acidulated with muriatic acid; it is then set upon a sheet of white paper, and the solution of permanganate of potash dropped into it, whilst stirred, until the completion of the reaction is indicated by the commencement of a reddish-yellow coloration of the fluid. If the experiment be several times repeated, the results will be found to agree very exactly. This testing of the solution of the permanganate must precede every new series of experiments on account of the readiness with which it undergoes change.

If it be wished to test an impure ferrocyanide of potassium to ascertain the amount of pure ferrocyanide contained in it, 5 grms. are dissolved in sufficient water to make 250 cub. centims., and 10 cub. centims. of this are taken and tested as above. If 80 degrees of the burette have been employed in the determination of the value of the solution of permanganate of potash, and 70 are now found to be sufficient, the statement 80 : 20 = 70 : x shows the amount of pure ferrocyanide in the substance under examination. Even this little calculation may be avoided by diluting the solution of permanganate of potash to such an extent, that 100° of it may exactly represent 0·200 grm. of ferrocyanide of potassium.

When the quantity of ferridcyanide of potassium in a compound

which contains no ferrocyanide is to be determined, 5 grms. of it are to be dissolved to form 250 cub. centims. of solution; 10 cub. centims. of this are to be measured off, from 5 to 8 cub. centims. of concentrated solution of potash added to them, the whole heated to boiling in a small dish, and 0·4 to 0·5 grm. of finely pounded oxide of lead added to it. This immediately acquires a brown colour, becoming partially converted into peroxide. The reduction is soon completed, and the change in the colour of the solution leaves no doubt as to when this has taken place. The contents of the dish are now diluted with water, filtered, the filter washed, and the whole diluted so as to amount to 250 cub. centims.; it is then acidulated with muriatic acid, when a strong white turbidity is produced by the separation of ferrocyanide of lead. The solution of permanganate of potash is now added, without paying any attention to the lead salt. The precipitate is dissolved in proportion as the ferrocyanogen is converted into ferridcyanogen; and the completion of the reaction is indicated, not only by the change of colour, but also by the restoration of perfect clearness to the fluid. No other method which could be devised for the reduction of the ferridcyanide of potassium furnished such good results as that just mentioned. Repeated experiments gave perfectly satisfactory results. It is only necessary to observe that the fluids must be concentrated.

Lastly, in the analysis of a substance containing both ferro- and ferridcyanide of potassium, the solution is to be prepared as above described; 10 cub. centims. are then tested without any further treatment, and another similar quantity after previous reduction. The first determination gives the ferrocyanide of potassium; the second gives this together with the ferridcyanide.

As 2 equivs. of crystallized ferrocyanide of potassium, =5281, represent 1 equiv. of ferridcyanide, =4117, the amount of the latter is obtained when the difference of the two determinations expressed as crystallized ferrocyanide of potassium is multiplied by 0·7795.

The reaction upon which this method is founded takes place according to the formula $10(Cfy, 2H) + Mn^2 O^7 + 2ClH = 5(2Cfy, 3H) + 2MnCl + 7HO$. This appears directly from the following experiments:—

5·1065 grms. of pure crystallized ferrocyanide of potassium were dissolved in 260 cub. centims. of water. Every 10 cub. centims. of this solution, containing 0·1964 grm. of the salt, were then tested by the above method. The average of these almost exactly concordant experiments gave 6·15 cub. centims. of a solution of permanganate of potash, of which 50 cub. centims. oxidized 0·219 grm. of pianoforte wire dissolved in muriatic acid. If we calculate 99·7 per cent. of iron in this, it represents 0·2183 grm.; the 0·1964 grm. of ferrocyanide of potassium therefore represent 0·02603 grm. of iron, which would require 6·0 cub. centims. of the solution of permanganate of potash for its oxidation. Consequently equal quantities of permanganate of potash are required for the oxidation of equivalents of ferrocyanide of potassium and iron, for the numbers 6·15 and 6·0 may be regarded as equal. Now as 10 equivs. of iron are converted

from protoxide to peroxide by 1 equiv. of permanganic acid, it is evident that 10 equivs. of ferrocyanide of potassium are oxidized by 1 equiv. of the same acid.

The following examples may serve to show the exactness of the method:—

1. 0·3865 grm. of pure ferrocyanide of potassium were dissolved in water, and treated as above. It required the employment of 29° of a solution of permanganate of potash, of which 74°·7 represented 1 grm. of the ferrocyanide. The 29° represented 0·3882 grm. of ferrocyanide, =100·4 per cent.

2. 0·7070 grm. of ferrocyanide of potassium, similarly treated, required 52°·6 of the solution, representing 0·7041 of ferrocyanide of potassium, =99·6 per cent.

3. 5·3379 grms. of pure ferridcyanide of potassium were dissolved in 250 cub. centims. of water. Every 10 cub. centims. of this solution, after reduction, required for their oxidation 8·4–8·35–8·35 of a solution of permanganate of potash, of which 6·05 cub. centims. represented 0·1964 grm. ferrocyanide of potassium. 8·37 cub. centims. therefore represent 0·2717, =0·2118 of the ferridcyanide. 250 cub. centims. consequently contain 5·2950 grms., =99·2 per cent.

4. 0·3410 grm. of ferridcyanide of potassium were treated as in the preceding experiment. Its oxidation required 32°·5 of the solution of permanganate of potash employed in experiments 1 and 2. The 32°·5 therefore represent 0·43508 of ferrocyanide of potassium, or 0·3391 grm. of the ferridcyanide, =99·44 per cent.—Liebig's *Annalen*, xc. p. 160.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Liverpool, September 20th, 1854.

Chemical Examination of some Alloys of Copper and Zinc.

By D. Forbes, F.G.S., Ass. Inst. C.E.

The nature of alloys is as yet so imperfectly understood, that every attempt to extend our knowledge in that department of chemistry is of interest; and under this impression, the chemical examination of an alloy of copper and zinc formed accidentally is now laid before the Association.

Whilst a number of brass castings were being made of ordinary brass, the precise proportion of the two metals employed being uncertain, from the fact of some old brass being at the same time used, and the mixture being left entirely to the workman's judgement, it was found that on cooling one of the castings had split into several pieces, presenting an appearance in many parts quite striking, and totally different from the brass which composed the other castings, although all of them had been poured into their moulds out of one

crucible of melted metal, so that the same appearance would be ordinarily expected.

The others appeared similar in all respects to ordinary yellow brass; whilst this, on the contrary, when broken, showed in most parts a brilliant silvery white fracture, and was so brittle that it shivered to fragments when gently struck with a hammer. This white alloy was surrounded by a thin envelope or skin of yellow brass, which on the one side of the coating showed itself in greater quantity, and nearly composed the whole thickness of the casting, presenting a yellow, corney, crystalline fracture, with occasionally more or less intimate intermixture of the white alloy.

It appeared evident, therefore, that some arranging chemical force had come into play; and deeming it of interest to know in what proportions the two metals were combined in this alloy, an analysis of each was made.

I. *The White Alloy.*

This was, when freshly broken, of the most brilliant silvery white colour imaginable, and probably equal, if not superior, in point of reflecting light, to speculum metal. It was extremely brittle, and could be easily reduced in a mortar to the finest powder, which then had a dark gray appearance.

The fracture is conchoidal; and the surface, when exposed some time to the air, tarnishes of a yellow colour.

The specific gravity at 60° F. was found to be 8·09.

It was soluble completely in hydrochloric acid, with evolution of hydrogen.

In order to see whether the determination of the copper present could not be conveniently made by Fuchs' method, 26·57 grs. were dissolved in a small bottle with glass stopper, filled up with pure hot water, and a small plate of pure copper, weighing 57·63 grs., placed in it; but it was found, even after two weeks' standing, that the solution was not decolorized, the plate of copper then having lost 11·19 grs., equivalent to 42·12 per cent. copper. As, however, this method did not succeed—

17·89 grs. were dissolved in hydrochloric acid; the strong acid solution was diluted and precipitated by sulphuretted hydrogen, the precipitate filtered off, well washed with water containing sulphuretted hydrogen, dried, incinerated, ignited with excess of carbonate of ammonia, and weighed. The zinc was then precipitated from the filtrate and determined.

The results obtained were—

Zinc	9·06
Copper	8·87
	17·93

which, expressed in per-centages, gives—

Zinc	50·64
Copper	49·62
	100·26

there being a slight excess from error.

Considering now the equivalent of copper as 31·66, and that of zinc at 30·30, these results closely approximate to the formula 1 equiv. zinc + 1 equiv. copper, which would give a per-centage composition of—

Zinc	50·51
Copper	49·49

It is probable however that the per-centage of copper here found is rather high, as on taking another portion of this alloy, 20·06 grs., dissolving it in hydrochloric acid, with addition of a little nitric acid to accelerate solution, and precipitating the strongly acid solution when previously diluted with water with sulphuretted hydrogen, washing, dissolving the sulphuret of copper in nitric acid, digesting until the sulphur was yellow, and precipitating the filtered solution by potash in excess and boiling for some time, then collecting the oxide of copper and determining it as usual, it weighed 11·69 grs. =9·33 metallic copper; and at the same time it was found that some zinc was present in the potash solution filtered off this oxide; and this possibly might have been the case in the previous analysis.

The results now obtained will give a per-centage of—

Copper	46·51
Zinc	53·49

which agree pretty well with the formula—

Copper	7 equivs.
Zinc	8 equivs.

or, in per-centage—

Copper	46·17
Zinc	53·83

which is most probably the real composition of the alloy.

II. *The Yellow Alloy.*

This alloy broke with a crystalline fracture, but was not brittle, and had the ordinary appearance of brass, except probably that instead of being fibrous in structure when broken across, it appeared granular and fractured without bending; a small portion of the purest, used for determining the specific gravity, afforded 7·94, and a large piece gave 8·00, but was not perfectly free from intermixture of the white alloy. It is consequently somewhat lighter in specific gravity than the white alloy.

20·04 grs., dissolved in hydrochloric acid, with a little nitric acid added; the acid solution diluted, precipitated by sulphuretted hydrogen; the precipitated sulphuret of copper then dissolved in nitric acid, and precipitated whilst boiling with excess of pure potash; the precipitate, perfectly washed and estimated, afforded 14·29 grs. oxide of copper, equivalent to 11·40 copper; and the per-centage calculated from this would be—

Copper	56·91
Zinc	43·09

which will closely agree with the formula $Cu^4 Zn^3$, which gives—

Copper	56·66
Zinc	43·34

and which is doubtless the constitution of the alloy.

There can be little doubt, judging from the above analyses, that these two alloys can be considered as—

$$Cu^7 Zn^8$$

and

$$Cu^4 Zn^3;$$

and it is very remarkable that an alloy containing so much copper as the former of them should be so entirely white and brilliant without the slightest tinge of yellow; whereas, according to Mallet's experiments, the alloys formed by him, even with so low a percentage as 32·8 of copper, were dark yellow in colour, this alloy being

$$Cu^1 Zn^2,$$

as also all the alloys mentioned by him as containing more copper.

I resolved therefore to see if I could reproduce this alloy, and first tried to make an alloy composed of $Cu^1 Zn^1$, by melting the copper, and adding when melted the proportional quantity of zinc in the solid form, but heated, adding however about 4 per cent. more zinc to allow for volatilization; I obtained an alloy which was of a yellow colour, broke with a strong grain, and appeared to be malleable, or somewhat so, whilst hot.

I then tried to form in a similar manner the alloy $Cu^4 Zn^3$, and found that a white alloy was produced, which, although not so brilliant as the one here analysed, would probably have been so if cooled under other circumstances, as it was more crystalline in texture. It however afforded full evidence of the identity of the alloys, and also proved how a very slight variation of the relative quantities of these metals do completely alter their appearance and physical properties.

An alloy of this description might, if obtained equally brilliant, be probably of use for specula or reflectors; although it tarnishes, still I am not aware whether this happens quicker than with specula metal.—*Communicated by the Author.*

On the Equivalency of Starch and Sugar in Foods.

By J. B. Lawes, Esq., F.R.S., *and* Dr. J. H. Gilbert, F.C.S.

At the meeting of the British Association at Belfast, the authors had given a paper on the composition of food in relation to respiration and the feeding of animals, in which they had illustrated, by reference to numerous experiments, that, as our current food-stuffs go, it was the amounts they supplied of the assimilable *non*-nitrogenous, rather than those of the nitrogenous constituents, which measured both the amount consumed by a given weight of animal within a given time, and the amount of increase obtained from a given weight of food. The results which formed the subject of the

present communication afforded further illustration of some of the points brought forward in the former one; but these new experiments, like the former ones, had been arranged with reference to certain practical questions, as well as to the more scientific bearings of the subject. Thus those interested in the growth of sugar had long wished to obtain the introduction of the lower qualities of that article, for *feeding purposes, duty free.* The subject of the remission of the malt tax, for the same object, had also frequently been agitated. According to the results of the experiments, numerous tables of which were exhibited in the room, and in which the animals (pigs) had been made to rely for about one-third of their total food upon the *starch* or *sugar* employed, it appeared that all but absolutely identical amounts of the dry substance of the starch and sugar thus tried against each other had both been consumed by a given weight of animal within a given time, and been required to yield a given weight of increase. The practical identity in feeding value, which had, from the known chemical relationship of the two substances, been hitherto assumed, was now therefore experimentally illustrated; and it doubtless only varied in point of fact with their slightly-varying per-centages of carbon. If then sugar have no higher feeding capacity than starch, the relative prices, weight for weight, of sugar duty free, and of the starchy grains generally used for feeding purposes, would afford an easy means of estimating the probable œconomy of the use of the former. At the price, *including duty,* of the coarse Penang sugar used in the experiments, it would cost three or four times as much as the starchy grains at the present time; and it should be remembered that these would also supply a considerable amount of the needed nitrogenous constituents of food. These new results too, so far as they can be supposed to apply, considering the difference between cane-sugar and the saccharine matter of malt, were consistent with direct experiments, published by the authors some time since, on the comparative feeding values of malted and unmalted grain. It was true that malt, and other saccharine matters, might serve in some degree to give a relish to the food, and thus induce the animals to consume more, which in "*fattening*" is always a consideration; but this incidental benefit could not counterbalance much increased cost. Indeed the general results of experiment were contrary to the conclusion, that an extensive use of malt for feeding purposes would be such a boon as had been supposed.

The proved practical equivalency of starch and sugar in food was also of interest in reference to some other of the views maintained by the authors in their former papers. Thus it had been shown that a fattening animal assimilated much less nitrogen than had usually been estimated, and that, on the other hand, it might store up very considerably more fat than existed ready formed in its food; whilst this *produced* fat was doubtless in a great measure formed from the starchy and saccharine substances, which constitute so large a proportion of the *non*-nitrogenous constituents of our staple vegetable foods. It was these too which in practice served largely

to meet the requirements of the respiratory function, which, it had been shown, under ordinary circumstances, measured to such an extent the amount of food demanded by the animal system.—*Abstract, communicated by the Authors.*

On a Method of Analysis applicable to the Quantitative Estimation of Nitric and Acetic Acids. By J. H. Gladstone, F.R.S.

A good method for estimating the amount of nitric acid present in its compounds, or in mixtures of salts, has long been a desideratum. That which I propose bringing before the notice of the British Association is one which I have frequently made use of; and although it does not give rigidly accurate results, I have found it sufficiently exact for most purposes.

The process is as follows:—Place a weighed portion of the substance to be analysed in a small tubulated retort, and dissolve it in a little water. It will be remembered that all neutral nitrates are soluble; the few sub-nitrates which are insoluble in water should be reduced to a very fine powder. Add to the solution in the retort a large quantity of strong sulphuric acid, very many times more than is requisite to effect the decomposition of whatever nitrates may be present. Attach to the beak of the retort, in such a way as to preclude the escape of any gas, a receiver containing water and a considerable quantity of carbonate of baryta. Heat the liquid in the retort gently at first, but more strongly towards the end of the operation. The nitric acid of course distils over, and will be condensed wholly in the receiver, which, together with the neck of the retort, should be kept cool. There it will decompose the carbonate, forming nitrate of baryta, while the liquid will be ever ready to absorb or receive fresh increments of acid. The distillation should be continued till the sulphuric acid itself rises in vapour, sweeps down the nitric acid which may be adhering to the neck of the retort, and shows itself in the receiver by the production of a dense white cloud, from its decomposing some of the nitrate of baryta in solution. This decomposition is of no moment, as the nitric acid thus set free immediately decomposes in its turn an equivalent of the carbonate of baryta. The liquid must be boiled in order to agglomerate the sulphate, and to cause the deposition of any carbonate of baryta that may be dissolved by the free carbonic acid. After filtering away the sulphate and undissolved carbonates, a clear solution of pure nitrate of baryta is obtained. This may be evaporated to dryness and weighed; or, as the salt is rather apt to decrepitate when heated, it will be found preferable to convert the nitrate into the sulphate, and from that to calculate the amount of nitric acid which passed over into the receiver.

The points which require special notice in this process are,—1st, the purity of the sulphuric acid employed; as commercial sulphuric acid frequently contains a trace of nitric acid, it must be tested before it is used; 2nd, the gentle heating of the mixture in the retort, when there is a good deal of nitric acid in it, in order to

prevent any chance of the formation of nitrous fumes; 3rd, the long-continued heating of the liquid, so as to ensure the distillation of as nearly the whole of the nitric acid as possible. The liquid should scarcely be allowed to boil, lest some portion of a salt should spring over, which, whatever it was, if soluble, would vitiate the experiment. When these precautions are properly attended to, a very good result is obtained. Known weights of pure nitre were tried; the amount of nitric acid found was not 1 per cent. less than the theoretical amount. Very small quantities of nitric acid, combined with other matters, can be determined with considerable accuracy in this way, as was proved when 0·2 gr. of nitre was mixed with phosphate and sulphate of copper and soda, and subjected to the same treatment.

It is self-evident that this process cannot be employed when there is some other acid mixed with the nitrate, which is volatile, and gives a soluble baryta salt; or, rather, the process would require to be modified to suit the particular case, and such modifications can generally be easily devised.

It will also be evident that this process may be applied equally well to to a number of other volatile acids. Most of these however may be estimated by simpler methods. Yet it is valuable as applied to acetic acid, a quantitative determination of which is often a matter of great difficulty. Its applicability to this has been proved by direct experiment. The process is identical with that previously described. The plan suggested does not involve any new principle, but is brought forward merely as a fair mode of overcoming one of the most common practical difficulties in analytical chemistry.—*Communicated by the Author.*

[To be continued.]

PATENT.

Patent granted to Frederick Crace Calvert, *for Improvements in the Treatment of Naphthas and other Volatile Hydrocarbons.*

The patentee finds that pure benzine, and some of the volatile hydrocarbons obtained by the dry distillation of bituminous coals and shales, which also contain benzine, possess to a high degree the property of dissolving fatty or oily matters; and he proposes to apply this property of benzine to various useful purposes, hereinafter described. In order to render the various products that contain benzine suitable for their several applications, he submits them to the following treatment, the object of which is to destroy or remove some of the carburetted hydrogens which are mixed with them, and which, not being sufficiently volatile, interfere with the application of benzine.

He takes coal and shale naphtha (preferring for this purpose the limpid coal naphtha of commerce), and puts it in a suitable earthenware or leaden vessel, and adds to it sulphuric acid in small quantities until no more coloration is produced; consequently the quan-

tity of acid employed will vary with the relative degrees of purity of the coal or shale naphtha.

The naphtha so treated he then washes with pure water, or with a solution of an alkali, and submits it to distillation in an ordinary still. These operations are to be repeated until it is sufficiently pure for the various purposes to which it may be applied. For certain purposes, on a large scale, as hereinafter applied, it is only necessary to take a commercial coal naphtha, and distil it at a temperature which does not exceed 212° F.

The first application that is made of the purified coal naphtha or nearly pure benzine, is for the removal of spots and stains caused by fatty or oily matters, tar, paint, wax, or resin from cotton, woollen, silk, and other fabrics; and, owing to its great volatility, no mark or permanent odour remains on the fabrics operated upon.

The second application of the purified coal naphtha or nearly pure benzine, is for the removal of fatty or oily matters from hair, furs, feathers and wools, and to the cleaning of gloves and other articles made of leather, hair, fur and wool.

The third application of the purified coal naphtha or nearly pure benzine, is for removing the fatty matters which exist naturally in wool.

The fourth application of the purified coal naphtha or nearly pure benzine, is for the removal from wool of tar, paint, oil, grease, and similar substances, which are used by farmers for marking, salving, and smearing their sheep.

The fifth application of the purified coal naphtha or nearly pure benzine, is for cleansing or removing the oily or fatty matters which are contained in cotton waste that has been used for cleansing or wiping machinery, or other articles to which oil or grease has been applied.

To effect the several applications above named, purified coal naphtha or nearly pure benzine is simply applied to articles of small size by rubbing them with it; but, for other things of a larger size, the several articles and fabrics to be operated upon are placed in a suitable vessel, and the purified coal naphtha or nearly pure benzine is allowed to flow into the vessel; and, after leaving them in contact for several hours, the fluid is run off, and the articles and fabrics are passed through squeezers, and the yarn is submitted to pressure, so as to remove a great portion of the purified coal naphtha or nearly pure benzine containing the paint, tar, grease, oily or fatty matters in solution, and which is separated from the liquids by distillation in a suitable vessel. The greasy, oily or fatty matters, so obtained, may be applied in lubricating machinery and locomotive engines, and for other similar purposes.

The sixth application of this purified coal naphtha or nearly pure benzine is for making furniture paste.

To effect this object, 1 part of wax and 1 of resin is dissolved to 2 parts of purified coal naphtha or nearly pure benzine, by the aid of heat, until the whole is dissolved. It is then allowed to cool, and the paste is fit for use.—Sealed Dec. 27, 1853.

THE CHEMICAL GAZETTE.

No. CCLXXXIX.—November 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on some new Organic Radicals containing Arsenic. *By* MM. CAHOURS *and* RICHE.

IN the conclusion of a note on stanmethyle, which we laid before the Academy on the 6th of June 1853*, we announced that by the action of free arsenic upon the iodides of methyle and æthyle, combinations were formed containing carbon, hydrogen, arsenic and iodine; and that when arseniuret of potassium is substituted for the free arsenic, a great elevation of temperature is produced, whilst a body of a most nauseous arsenical odour passes by distillation. M. Landolt having recently published some researches regarding the action of iodide of æthyle upon arseniuret of sodium, we shall not recur to this subject, the results obtained by us being exactly in accordance with those of that chemist; and we shall confine ourselves in the present note to the compounds resulting from the reciprocal action of iodide of methyle and arseniuret of sodium.

When iodide of methyle is allowed to fall in small quantities into a small flask filled with carbonic acid, and containing at the bottom a little arseniuret of sodium in powder, a considerable amount of heat is disengaged; and if the additions of iodide of methyle be repeated until they no longer produce any elevation of temperature, and the mixture be then distilled in a current of carbonic acid, four products are obtained, namely, unchanged iodide of methyle, a white crystallized substance, and a heavy liquid composed of two different products. This liquid, which is only obtained in small quantity, even when operating upon a hundred grammes of materials, is a mixture of two products, of which one, boiling at about 248° F., corresponds with stibmethyle, and with the phosphuretted alkali of M. Paul Thénard; the second, which boils at about 329° to 338° F., possesses all the properties of cacodyle, with which it also agrees in composition. The crystallized substance consists of the iodide of a radical analogous to stibmethylium; this compound is formed in considerable quantity during the reaction, of which it is the principal product.

This substance separates from its saturated solution in iodide of methyle, in the form of magnificent laminæ of great brilliancy; its analysis gave the following results:—

0·408 grm. of the substance gave 0·166 water and 0·273 carbonic

* See Chem. Gaz., vol. xi. p. 292.

acid, which gives 4·59 per cent. of hydrogen and 18·53 of carbon, leading to the formula $(C^2 H^3)^4$ As, I. Thus,—

Carbon.....	8 =	48	18·32
Hydrogen	12	12	4·57
Arsenic	1	76	29·01
Iodine	1	126	48·10

When boiled with freshly-precipitated oxide of silver, the substance is decomposed, furnishing a strongly alkaline liquid, which when evaporated *in vacuo* gives very deliquescent crystalline laminæ, consisting of the hydrated oxide of the radical arsenmethylium; with nitrate or sulphate of silver, the solution of iodide of arsenmethylium gives by double decomposition the iodide of the metal and nitrate or sulphate of oxide of arsenmethylium. These compounds, which are very soluble and exceedingly deliquescent, separate in a fine crystalline form when their solutions are evaporated *in vacuo*; on analysis they gave numbers corresponding with the formulæ—

$$NO^5 (C^2 H^3)^4 AsO,$$

and

$$SO^3, (C^2 H^3)^4 AsO.$$

If we compare the formula of iodide of arsenmethylium with that of iodide of cacodyle, we shall see that the former only differs from the latter by containing 2 additional equivs. of methyle. If we consider besides, that in the reaction of iodide of methyle upon arseniuret of sodium, only a very small quantity of cacodyle is formed, whilst a considerable proportion of arsenmethylium is produced, it becomes probable that the latter would be formed by the action of iodide of methyle upon cacodyle. To verify this assertion, we put into a tube some cacodyle and iodide of methyle. Scarcely had the liquids come in contact when a violent reaction ensued, and a mass of crystals of a yellowish-white colour was obtained, impregnated with an oily matter of the same colour. The crystals, freed from the oil by draining and pressure between blotting-paper, dissolve in iodide of methyle with the addition of alcohol, and separate from this solution in the form of beautiful, colourless, tabular crystals, perfectly identical with those formed by the mutual action of arseniuret of sodium and iodide of methyle. When analysed, these crystals gave the following results:—

0·529 gr. gave 0·221 water and 0·286 carbonic acid, which gives 4·64 per cent. of hydrogen and 18·17 per cent. of carbon, leading naturally to the formula $(C^2 H^3)^4$ As, I.

These numbers clearly show the identity of this substance with that obtained with iodide of methyle and arseniuret of sodium. The solution of these crystals, when decomposed by oxide, nitrate, or sulphate of silver, furnished compounds which proved on analysis to be perfectly identical with those previously obtained. When the yellowish oily fluid was treated with water and dried *in vacuo*, it boiled at about 320° F. Its analysis gave the following results:—

0·422 gr. of substance gave 0·113 water and 0·168 carbonic acid,

which gives 2·9 per cent. of hydrogen and 10·85 per cent. of carbon. These numbers agree with the formula $C^4 H^6 As, I$, which is that of iodide of cacodyle. This reaction may be explained in the following manner:—

$$2(C^2 H^3 I)+2(C^4 H^6 As)=(C^2 H^3)^4 As, I+C^4 H^6 As, I.$$

Bromide of methyle acts powerfully upon cacodyle, and furnishes in like manner a beautiful, deliquescent, crystallized substance (bromide of arsenmethylium), and a liquid of a repulsive odour (bromide of cacodyle).

If iodide of æthyle be substituted for the iodide of methyle, no change is produced at the moment of mixing the materials; but if the mixture be left standing, a great abundance of magnificent crystals are gradually deposited, consisting of the iodide of a new radical containing 2 molecules of methyle and 2 molecules of æthyle combined with 1 molecule of arsenic. This radical, to which we shall give the name of *arsenmethylæthylium*, corresponds with arsenmethylium, in which 2 molecules of methyle are replaced by 2 molecules of æthyle; an oil is formed in this reaction, which, like the preceding, boils at 320° F., and possesses, like it, the composition of iodide of cacodyle. Thus—

$$2(C^4 H^5 I)+2(C^4 H^6 As)=(C^2 H^3)^2 (C^4 H^5)^2 As, I+C^4 H^6 AsI.$$

The solution of these crystals, treated with oxide of silver, furnishes a very alkaline liquid, which deposits on evaporation very deliquescent scaly crystals, consisting of oxide of arsenmethylæthylium—

$$(C^2 H^3)^2 (C^4 H^5)^2 As, O.$$

The solution of this iodide also gives with nitrate and sulphate of silver, iodide of silver and a well-crystallized, but very deliquescent sulphate and nitrate, of which the composition is represented by—

$$NO^5, (C^2 H^3)^2 (C^4 H^5)^2 As, O,$$

and

$$SO^3, (C^2 H^3)^2 (C^4 H^5)^2 As, O.$$

Bromide of æthyle acts a little more slowly than the iodide upon cacodyle, and furnishes in the same manner bromide of arsenmethylæthylium and bromide of cacodyle.

Muriatic æther mixes very readily with cacodyle; but this liquid, when placed with cacodyle in a sealed tube and left for several days, does not appear to act upon it at ordinary temperatures. But if this tube be heated to 356°–392° F., an oil soon separates, which settles to the bottom of the tube, and goes on increasing gradually in quantity; it contains some long colourless needles. If this be distilled, collecting only the first half that comes over, the remainder on cooling furnishes a larger quantity of the preceding crystals, which are very deliquescent, and consist of chloride of arsenmethylæthylium—

$$(C^2 H^3)^2 (C^4 H^5)^2 AsCl.$$

A solution of bichloride of platinum poured into the watery solution of this chloride, gives a yellow precipitate, which dissolves at the temperature of ebullition of a mixture of equal parts of water

and alcohol, and is deposited again on cooling in beautiful needles of a reddish-orange colour.

Bichloride of mercury with this chloride furnishes a colourless crystalline compound, in the form of small, white, satin-like needles. Chloride of gold gives small needles of a golden-yellow colour.

The liquid which passed by distillation in the preparation of the chloride of arsenmethylæthylium, boils at about 221° F. It possesses exactly both the properties and composition of chloride of cacodyle.

Sulphuret of æthyle acts in a similar manner upon cacodyle, but only with the aid of heat, and then very slowly; it gives sulphuret of arsenmethylæthylium, crystallizing in a yellowish oil (sulphuret of cacodyle).

Iodide of amyle, heated with cacodyle, only reacts upon it when kept for two or three days at a temperature of 356° F.; it gives rise to very brilliant, pearly, broad, and very thin tabular crystals, floating in an oily liquid, which boils at 320° F.

These crystals, well dried *in vacuo*, are composed of iodide of arsenmethylamylium—

$$(C^2\,H^3)^2\,(C^{10}\,H^{11})^2\,As,\,I.$$

The oil presents all the properties of iodide of cacodyle.

This new iodide, like the preceding, furnishes with oxide, nitrate, and sulphate of silver the iodide of that metal, and oxide, nitrate, and sulphate of arsenmethylamylium, the constitution of which is expressed by the following formulæ:—

$$(C^2\,H^3)^2\,(C^{10}\,H^{11})^2\,As,\,O,$$
$$(C^2\,H^3)^2\,(C^{10}\,H^{11})^2\,As,\,O,\,SO^3,$$

and

$$(C^2\,H^3)^2\,(C^{10}\,H^{11})^2\,As,\,O,\,NO^5.$$

When iodide of methyle is heated with metallic arsenic to a temperature of about 392° F., the latter disappears, and a large quantity of reddish-orange crystals is obtained; these are in broad tables, moistened with a brownish liquid; when dried between paper, they gave the following results:—

0·402 gr. of substance furnished 0·072 gr. of water and 0·098 gr. of carbonic acid, which gives 1·98 per cent. of hydrogen and 6·65 per cent. of carbon. These numbers lead to the formula $(C^2\,H^3)^4\,As,\,I,\,AsI^3$, which would make this a compound of iodide of arsenic and iodide of arsenmethylium. If these crystals be distilled, they are destroyed, and furnish an oil of a penetrating odour, which excites tears. It is a mixture of several substances; the least volatile, which boils at 338° F., possesses the composition of iodide of cacodyle; if it be distilled with an amalgam of zinc, it gives a colourless liquid of a strong arsenical odour, which takes fire in the air, and possesses all the properties of cacodyle. The more volatile portion, which did not give us concordant results on analysis, deposits long white needles of great beauty, which are isomeric with iodide of cacodyle.

Iodide of æthyle, heated with arsenic, gives, like iodide of me-

thyle, splendid red tabular crystals, the composition of which is analogous to that of the crystals furnished by the latter, and leads to the analogous formula $(C^4 H^5)^1 AsI, AsI^3$. When distilled, these crystals are decomposed, furnishing a liquid which begins to boil at 320° F., and the last portions of which pass over at about 572° F. When this product is again distilled, a considerable proportion is collected between 356° and 374° F. The analysis of this compound gave numbers leading to the formula $(C^4 H^5)^3 AsI^2$.

Distilled with an amalgam of zinc, a liquid and some fine crystals are obtained; the liquid, which has an insupportable odour of arseniuretted hydrogen, boils at 284° F., and its composition may be represented by the formula $(C^4 H^5)^3 As$; it is evidently the arsentriæthyle of Landolt.

The crystals dissolve in alcohol, and separate therefrom in the form of long silky needles; this compound possesses exactly the constitution of iodide of arsentriæthyle.

Between 442° and 459° F., a considerable quantity of a liquid of an insupportable odour passes, which furnished on analysis numbers leading to the formula $(C^4 H^5)^2 AsI$. This compound, distilled with amalgam of zinc, furnishes a liquid boiling at 392° F., which possesses the composition of the arsendiæthyle or æthylic cacodyle of M. Landolt. The alcoholic solution of this compound, treated with nitrate and sulphate of silver, gives iodide of silver and a well-crystallized nitrate and sulphate, which are expressed by the formulæ—

$$NO^5 (C^4 H^5)^2 AsO, HO,$$

and

$$SO^3 (C^4 H^5)^2 AsO, HO.$$

To resume, we find that the iodides of methyle and æthyle, when acting upon arsenic at 392° F., furnish definite crystalline products, which may be considered as compounds of iodide of arsenic with iodide of arsenmethylium or arsenæthylium. When distilled, these products are decomposed, furnishing—

In the first case, iodide of arsendimethyle or cacodyle, and probably iodide of arsentrimethyle.

In the second, iodide of arsendiæthyle and iodide of arsentriæthyle.

When arseniuret of potassium or sodium is substituted for the arsenic, these iodides disappear, to give place to their radicals; iodides of arsenmethylium and arsenæthylium are also produced. Iodide of amyle gives similar results.

By these reactions we have settled beyond a doubt the true constitution of cacodyle, and we have shown that by its reaction upon the chlorides, bromides, iodides, and sulphurets of methyle and æthyle, it gives rise to similar compounds of new radicals, which furnish a series of salts, in the complete investigation of which we are now engaged.—*Comptes Rendus*, Sept. 18, 1854, p. 541.

On the Identity of Peucedanine with Imperatorine.
By R. Wagner.

The author prepared imperatorine according to Wackenroder's process, by the extraction of the root of *Imperatoria Ostruthium*

with æther. After the volatilization of the æther, the imperatorine separates. It is rendered purer by recrystallization from æther and cold alcohol, in which the fatty oil is only slightly soluble, but it still retains a burning taste. The author therefore boiled it with thick milk of lime, when a lime-compound is produced, which forms caseous flakes; this is decomposed by acetic acid, and the imperatorine, which is precipitated in brown flakes, is purified by recrystallization from cold alcohol. It is then perfectly tasteless.

The author afterwards gives the following process of his own for the preparation of imperatorine, by which a greater proportion is obtained. In this way he prepares imperatorine both from the root of *Imperatoria Ostruthium* and from *Peucedanum officinale*. For this, 1 kilogrm. of finely-cut air-dried root is extracted, in a displacement apparatus, with 3 litres of alcohol of spec. grav. 0·876, at the ordinary temperature. Through the extracted root 1 more litre of alcohol is then passed; and this is followed by a litre of water, so as completely to remove the alcohol. The extracts are mixed and evaporated on the water-bath, or in a retort, at a temperature of about 140° F., until about 1 litre of fluid remains. The fluid, when left to stand, separates into two strata,—a thicker, pale brown, watery one at the bottom, which has a sweet and aromatic taste; and a superior resinous one, of a brown colour. The latter is separated from the watery stratum, and placed in a broad porcelain saucer. In a few days it becomes converted into a granular crystalline mass, which is pressed between blotting-paper to remove the fatty oil, which has the greatest affinity to linseed-oil, acquires a yellow colour with potash, at the same time evolving the characteristic odour of linseed-oil. The granular mass thus obtained is purified by treatment with milk of lime and recrystallization from cold alcohol. In this process only a small quantity of the fatty oil is dissolved; this being a good solvent for imperatorine, produces a loss.

The watery fluid contains besides a great deal of grape-sugar, a small quantity of a nitrogenous body, which when heated with potash evolves an odour like that of coniine.

The author has compared the product prepared by him with a sample sent to him by Prof. Wackenroder; the differences which occur in the properties attributed to peucedanine and imperatorine arise from adherent impurities. The pure substance is tasteless. Prof. Wackenroder has informed the author that imperatorine can only be prepared from old roots of *Imperatoria*; and this the author has found to be perfectly correct. In operating upon strong-smelling fresh roots, the author never obtained anything but a sticky mass, without any trace of crystallization, and it was only by employing old roots that he procured crystallized imperatorine. This circumstance seems to indicate that the ætherial and fatty oils contained in such abundance in the fresh roots assist in the formation of the crystallized imperatorine. The analysis of imperatorine gave,—

Carbon	70·06	70·21	24	70·50
Hydrogen	6·19	6·48	12	5·89
Oxygen	..	..	6	23·52

Peucedanine is resolved, by treatment with alcoholic solution of potash, into angelicic acid and oreoseline.—*Journ. für Prakt. Chem.*, lxii. p. 275.

Note on the Electrolytic Production of the Earthy and Alkaline Metals. *By* R. Bunsen.

In a previous memoir* I have described the method by which the metal magnesium, first prepared by Wöhler, may be obtained by an electrolytic process in reguline masses of the weight of a gramme, putting off further particulars as to the application of this method to the preparation of the earthy metals to another occasion. Although M. Deville has since been engaged upon the same subject, and especially upon the preparation of Wöhler's aluminium on a large scale, it does not appear superfluous to me to give a short notice of the process by which aluminium may be prepared in large reguline masses by my method, and even still more easily than magnesium, if one of the well-known double chlorides of aluminium be employed in the reduction, this possessing the necessary fusibility for the electrolysis.

The chloride of aluminium may easily be prepared by the pound in the following manner:—Alumina is prepared by the calcination of sulphate of alumina and ammonia, or of the sulphate of alumina, which is now common in the shops; or according to Liebig's process, from alum and chloride of barium; it is mixed with the corresponding quantity of charcoal, and put into a common wide-necked retort, capable of holding from $1\frac{1}{2}$ to 2 litres, which is then covered with a *thick* coating of clay and forge-scales, and so placed in a large furnace that the neck may project in a horizontal direction from 3 to 5 inches from the aperture of the furnace, which is to be closed up with clay. The neck of a second similar glass retort is passed over this neck, so that the whole forms two horizontal retorts united by their necks without luting, of which the one in the furnace serves for the production and sublimation of the chloride of aluminium, and the other for the reception of the sublimed chloride. To enable the chlorine to be introduced into the alumina, the retort serving as a receiver is bored through in a line with the axis of the two necks by means of the point of a triangular file moistened with oil of turpentine, and the aperture enlarged by a round file moistened with turpentine, until a *wide* tube of hard glass (a common combustion-tube is the best), serving for the passage of the chlorine, may be passed through the two necks into the mixture of alumina. The retort in the furnace is first brought to a *slight* red heat, and a current of chlorine, washed with water and well dried, is then passed into the mixture. The formation and sublimation of the chloride of aluminium takes place readily and completely, so that half a pound of the chloride may easily be collected in the receiver in a few hours†.

* Chem. Gaz., vol. xi. p. 114.

† It is scarcely necessary to observe, that other chlorides, such as chloride of pelopium, may also be most easily prepared in large quantities in this manner.

If the chloride thus obtained be heated in a digesting flask with an equivalent proportion of fused pulverized chloride of sodium, the well-known chloride of aluminium and sodium, which fuses at a temperature far below 392° F., is obtained, from which the aluminium may be reduced by the method described in my memoir upon magnesium. As the metal is separated in a pulverulent form at a low temperature, a sufficient quantity of pulverized fused chloride of sodium is introduced into the mixture during the electrolysis, to enable the temperature to be raised at last nearly to the fusing-point of silver. At the close of the experiment, the metal is found in the cold chlorine compound in large reguline globules, which may be fused together into a regulus by dropping them into fused chloride of sodium at a white heat; this may be hammered out into plates of an inch square. Reguline aluminium alone possesses the properties described by M. Deville; the pulverulent form decomposes water exactly as was observed by Wöhler with the product reduced by potassium. There is consequently no reason for considering the metal first prepared by Wöhler as an impure product.

We may soon expect an interesting memoir upon the preparation of sodium, calcium, &c., with which Dr. Mathiessen of London is now occupied at Heidelberg. The great difficulties which stand in the way of the electrolytic production of these metals have been partially overcome by this zealous young chemist. Dr. Mathiessen has already succeeded in reducing sodium, over the spirit-lamp, by means of a current produced only by four carbon and zinc elements, and in such quantities as to be beaten out, under naphtha, into plates of a line square. The reduction takes place so easily, that it will henceforward be considered as one of the simplest college-experiments.—Poggendorff's *Annalen*, xcii. p. 648.

On Glucina. By J. Weeren.

The author has instituted a further investigation of glucina. In the first portion of his memoir, he treats of the methods of separating glucina from alumina. He finds,—

1. That carbonate of ammonia dissolves not only glucina, but also considerable quantities of alumina.

2. That glucina is not completely precipitated from its solution in potash by dilution and boiling.

3. That Berthier's method of separation (by sulphurous acid) is attended by numerous imperfections.

4. The method of separation proposed by Berzelius is the only practicable one. In this the earths are boiled with solution of muriate of ammonia until no more ammonia is evolved; the glucina is dissolved, the alumina remains undissolved. This method gives exact results when,—1st, the two earths are precipitated only after the addition of a very concentrated solution of muriate of ammonia; 2nd, the mixture is only boiled for a short time; 3rd, too great an evaporation of the fluid is avoided; and 4th, the glucina is finally precipitated with sulphuret of ammonium, instead of with ammonia.

5. Hydrate of alumina does not decompose a concentrated solution of muriate of ammonia at a boiling heat, nor is it taken up by carbonate of ammonia.

6. Glucina is partially precipitated by carbonate of baryta from solutions of its salts, even at a very low temperature; so that baryta cannot be employed to separate it from alumina.

In the second part of his memoir, the author gives the facts in relation to glucina, which lead him to the following conclusions:—

1. Hydrate of glucina contains, for every equivalent of oxygen in the base, 1 equiv. of oxygen in the hydrate-water.

2. It is very readily decomposable, and loses a part of its water apparently even at 230° F.

3. Hydrate of glucina, when dissolved in concentrated solution of potash, is not completely precipitated by dilution with water; the portion separated contains potash, from which it may be freed by washing, when it has again the property of dissolving in concentrated solution of potash.

4. It is somewhat soluble in an excess of ammonia.

In the third part, the author gives the following information respecting carbonate of glucina:—

1. Carbonate of glucina has a variable composition, according as it is,—1st, separated by boiling from its solution in carbonate of ammonia; or, 2nd, precipitated by carbonate of ammonia. The latter is a mixture of carbonate with hydrate of glucina.

2. Carbonate of glucina loses carbonic acid by boiling with water, becoming partially converted into hydrate of glucina; when exposed to a temperature of 212°–230° F. in a current of dry air, it loses no carbonic acid; it is soluble in an excess of carbonate of ammonia.

In the fourth division, the author gives the facts relating to sulphate of glucina, which lead him to the following results:—

Sulphate of glucina,—

1st, is readily soluble in water, but insoluble in alcohol;

2nd, loses 4 atoms of its water at 95° F., and crumbles to pieces; at 212° to 230° F. it still retains 1 atom of water, but loses its white colour, and forms a gray crystalline powder;

3rd, loses no sulphuric acid at 302° to 392° F.;

4th, the gray crystalline mass produced in the preparation of sulphate of glucina contains only constitutional water.

In his last division, the author details a series of experiments, made with a view to the determination of the atomic weight of glucina. He determined the amount of the earth in pure sulphate of glucina, and found,—

		Calculated	
grm. glucina.	grm. SO^3.	as BeO.	as Be^2O^2.
0·3163	1·0071	157·04	471·10
0·2872	0·9057	158·56	475·68
0·2954	0·9388	157·33	471·99
0·5284	1·6763	157·61	472·82
Average according to Weeren. . .		157·64	472·90
Average according to Awdejew . .		157·72	473·14

The author's determinations consequently agree very nearly with those of Awdejew, and he proposes to take the mean of the two averages as the atomic weight of glucina. We thus obtain for,—

		I.	II.
H=1	the atomic weight of glucinium=	4·61	and 6·92
O=100	the atomic weight of glucinium=	57·68	and 86·50

according as we regard glucina as BeO (I.) or Be^2O^3 (II.).—Poggendorff's *Annalen*, xcii. p. 91.

Note on the Industrial Employment of the Earthy Metals. *By* A. Chenot.

The great affinity of aluminium for carbon, with which it forms a very stable and exceedingly hard alloy, renders it very valuable in my system of manufacturing steel. It serves to fix the carbon in the metal, so that the same piece of steel may be heated and tempered several times without alteration.

Aluminium generally gives steels and alloys of great hardness, very white, dull, and damasked; these alloys are ductile and malleable. The alloys of silicium, on the contrary, have a short granular fracture, of a dull white, without lustre; they are excessively hard, but brittle, and become more and more so in proportion as the quantity of silicium is increased; 5 or 6 per cent. of silicium renders metals and alloys capable of being pounded like stones under the pestle.—*Comptes Rendus*, August 28, 1854, p. 428.

On the Preparation of Rouge as a Polishing Powder for Glass and Metals. *By* Prof. A. Vogel, Jun.

The author recommends the employment of oxide of iron obtained by the calcination of protoxalate of iron, in preference to the lixiviated colcothar, as a polishing powder for optical glasses, metals, &c., especially for the finer work. At the present price of sulphate of iron and oxalic acid, it may be prepared for about five shillings a pound.—Buchner's *Neues Repert.*, iii. p. 309.

ANALYTICAL CHEMISTRY.

On the Use of Hydrogen Gas and Carbonic Acid Gas, to displace Sulphuretted Hydrogen in the Analysis of Mineral Waters, &c. *By* Prof. W. B. Rogers *and* Prof. R. E. Rogers.

I. *On the Use of Hydrogen Gas in the Analysis of Sulphurous Waters.*

One of the most difficult points in the analysis of mineral waters is the determination of the sulphur, which is contained in many of

them in the two conditions of sulphuretted hydrogen and a sulphide, either of an alkaline metal or of magnesium or calcium. No satisfactory process has we believe yet been devised for this purpose. It is easy enough, by the nitrate of silver or chloride of copper, to determine the total quantity of sulphur present in these compounds; but in the subsequent process of boiling the liquid, preparatory to the precipitation of the sulphur of the sulphides, while we expel the free hydrosulphuric acid, we at the same time decompose the sulphide of magnesium or calcium which may be present, even when the process is conducted out of contact with the air, as in an atmosphere of hydrogen gas; and if we boil the liquid in the air, or even expose it for some time to the atmosphere at common temperatures, the sulphides of sodium and potassium, as well as of magnesium and calcium, are gradually decomposed by the carbonic acid of the air, evolving their sulphur in the condition of hydrosulphuric acid. At the same time, by the action of the atmospheric oxygen, a portion of the alkaline sulphide is converted into hyposulphite. It is therefore desirable to discover some method of separating the free hydrosulphuric acid, without at the same time affecting the other sulphur compounds present in the water. This we think we have attained by transmitting through the sulphurous water a stream of hydrogen gas. In repeated trials made with natural hepatic waters, among them the celebrated Blue Lick water of Kentucky, and with an aqueous solution of hydrosulphuric acid, prepared for the purpose, we have found that by continuing for a sufficient time the washing action of the hydrogen, we could reduce the sulphuretted hydrogen to an almost insensible trace. A volume of 25 cubic inches of the Blue Lick water, submitted to this action for one hour, retained only a minute fraction of the original charge, and in one and a half hour it gave only the slightest appreciable trace of sulphuretted hydrogen.

The hydrogen used for this purpose, before reaching the vessel which contains the mineral water, is conducted through a solution of potash, in order to remove any hydrosulphuric or carbonic acid it may contain. Thence it is made to pass into a second vessel containing the sulphurous water, through which it bubbles in a brisk but not violent stream. The gas, more or less charged with sulphuretted hydrogen, is led into a third vessel, containing either a solution of nitrate of silver to which ammonia has been added, or an alkaline solution of arsenious acid, to arrest the sulphuretted hydrogen. The former solution is greatly to be preferred, where the mineral water is only feebly sulphurous. The sulphur thus precipitated is to be determined in the usual way.

Suppose the mineral water to contain free hydrosulphuric acid, together with sulphides, say of potassium and magnesium, we may proceed as follows:—

1. We determine, for a given volume of the water, the total amount of sulphur present by the use of chloride of copper or nitrate of silver.

2. We subject an equal volume of the water to the hydrogen current until the escaping gas gives only the faintest trace of hydrosulphuric acid when the jet is received on a surface of white porcelain rendered moist by a mixture of nitrate of silver and ammonia. The mixed gas being passed into the silver or arsenious solution, gives a precipitate, from which we determine the amount of free hydrosulphuric acid in the water.

3. We apply heat to the flask containing the sulphurous water which has been thus treated, so as to cause gentle boiling, at the same time supplying the upper space with hydrogen in a moderate but steady stream. It will be found that below the point of ebullition, the issuing hydrogen will give scarcely a trace of hydrosulphuric acid; but as soon as the liquid begins to boil, the stream of vapour and hydrogen plainly shows the presence of this substance, then slowly evolved by the decomposition of the sulphide of magnesium or calcium.

4. We treat the remaining liquid with chloride of copper, or the arsenious solution, to determine the sulphur of the alkaline sulphide, which is the only sulphur compound left in the water. The sum of this and the sulphur of the free hydrosulphuric acid subtracted from the total quantity of sulphur, gives that of the sulphide of magnesium.

We find that a proportion of hydrosulphuric acid, too small to be quantitatively determined by precipitation from the water itself, can be ascertained by the use of the stream of hydrogen. It is only necessary to pass the gas which has been transmitted through the water into an ammoniacal solution of nitrate of silver in a long test-tube or Liebig's bulb. By continuing the action for one or two hours, we obtain a precipitate capable of being separated.

When the water contains no sulphide of magnesium or calcium, it is merely necessary, after determining the total amount of sulphur present, to boil the liquid in an atmosphere of hydrogen as long as the gas gives a distinct trace of SH by the tache on porcelain, as before described; and then by precipitation to determine the quantity of sulphur in the alkaline sulphide of the remaining liquid.

From what has been said, it is obvious that the only practical objection to the process here proposed, is the tardiness of the displacing action of the hydrogen gas; but considering the acknowledged imperfection of the methods in use, we think that it may be found worthy of adoption.

II. *On the Use of Carbonic Acid Gas in the Analysis of Mineral Waters containing Sulphuretted Hydrogen.*

As might be inferred from its great absorbability by water, carbonic acid acts much more rapidly than hydrogen in separating hydrosulphuric acid from that liquid. To assure ourselves of this effect, we made several experiments with natural and artificial sulphurous waters, all of which led to the same result. The following example will suffice to show the efficiency and promptness of the displacing action of the carbonic acid.

25 cubic inches of Blue Lick water, contained in a narrow-necked bottle, were subjected to the washing action of a brisk stream of carbonic acid gas, previously purified by transmission through water. In fifteen minutes the liquid, tested by ammoniacal nitrate of silver, gave a scarcely discernible trace of hydrosulphuric acid, and in twenty minutes not a vestige of it could be detected by the same reagent. The rapidity and completeness of the separation are as striking as the ease with which the experiment can be made.

When therefore a mineral water is known to contain sulphuretted hydrogen only in the free state, we would recommend, as the simplest and most exact method for determining this ingredient, to pass through the liquid a stream of washed carbonic acid gas, and to arrest the hydrosulphuric acid, by conducting the current of mixed gas into an ammoniacal solution of nitrate of silver in a small flask or Liebig-tube. The precipitated sulphuret being mingled with only a small volume of liquid, admits of more easy separation and determination than when formed in the usual way by adding a precipitant to a large mass of the mineral water. In the case of feebly sulphurous waters, this method is, we think, greatly superior in accuracy as well as promptness to any of those in use. By operating on a considerable volume of the water, the flask or tube will furnish the precipitated sulphuret in sufficient amount for a quantitative determination in cases where in the ordinary way no separable precipitate would be obtained.

As carbonic acid is capable of decomposing the sulphides contained in a mineral water, giving rise to free hydrosulphuric acid, it cannot be employed for determining the quantity of the latter when associated in the water with a sulphide. In this case the stream of carbonic acid would carry with it the hydrosulphuric acid due to its reaction with the sulphides, as well as that existing ready formed in the liquid. For such a water, hydrogen gas, used as above explained, is the proper displacing agent.—Silliman's *Journal*, Sept. 1854.

On a Chemical Process for the Quantitative Determination of Sugar. *By* E. Maumené.

When I laid before the Academy my process for the qualitative analysis of saccharine matters, founded upon the action of the chlorides, and especially of bichloride of tin ($SnCl^2, 5HO$), I did not expect to be able to ascertain the quantity of sugar by this reagent. But numerous experiments made since have enabled me to regulate its action, and to solve the difficult, and hitherto insoluble problem, of determining the quantity of sugar by a chemical agent*.

To regulate the action of chloride of tin upon sugar, all that is necessary is to employ a great excess of the former, 15 to 30 grms. of chloride to 1 of sugar. By evaporating the mixture to dryness, and then baking it for some minutes at 248° to 266° F., it becomes

* Fromherz's liquid, as is well known, only gives a rough approximation.

blackened, as I have described; but instead of being converted into a blackish-brown mass, formed of two parts, one soluble, the other insoluble, unequal in quantity and not in a constant proportion, the mixture gives a single, completely insoluble product, of which the formation may be very easily explained. Analysis shows that this blackish-brown body has the formula $C^{12} H^4 O^4$; it is sugar *minus* water, $C^{12} H^{11} O^{11} - 7HO = C^{12} H^4 O^4$. It is obtained with grape-sugar, cellulose, dextrine, &c., or generally with all the substances of the formula $C^a (HO)^b$.

The action of the bichloride is consequently a simple contest with the sugar, or analogous substances, for the preservation of the combined water. We may say that the chloride, $SnCl^2$, 5HO, or $SnCl^2$, 2HO, is in the presence of another hydrated body, $C^{12} H^4 O^4$, 7HO, and that, when the temperature is raised, the water is driven off from that body the affinity of which is weakest, that is to say, $C^{12} H^4 O^4$. For this body I propose the name of *carameline.*

The course to be followed in analysing a saccharine fluid is very simple. Suppose first that the liquid contains a single kind of sugar, and no other substance, of the formula $C^a (HO)^b$.

The quantity of sugar is first determined approximatively by means of an addition of several grammes of bichloride of tin; it is evaporated to dryness, with careful management of the temperature, and the product is heated for ten minutes to 248°–266° F., to convert the sugar into carameline. This is treated with water, when, if the action of the chloride be not complete, the water acquires a brown colour. In this case more chloride is added, the mixture evaporated, and heated as before to 248°–266° F. In general this product, when treated with distilled water, gives no colour. The sugar is then entirely converted into carameline, which is completely insoluble in water, acids and alkalies*. If the residue be washed with boiling water strongly acidulated with sulphuric or muriatic acid, so as to remove other matters, the carameline is obtained pure, or nearly pure. It is collected upon a filter, and its weight (P) determined

By the proportion $C^{12} H^4 O^4 : C^{12} H^{11} O^4 :: P : x$; x gives the

1350 2187·5

quantity of sugar. The second term is replaced by $C^{12} H^{12} O^{12}$ (2300), or by $C^{12} H^{10} O^{10}$ (2025), if grape-sugar or dextrine be under determination.

The operation just described sometimes shows exactly the quantity of sugar at once; but it is generally necessary to obtain more precision; the operation is then recommenced in the following manner:—

The same volume of liquid, the approximate value of which is now known, is taken, and for each gramme of sugar 15 to 30 grms. of bichloride are added to it. It is then evaporated, &c. The cara-

* Nitric acid and nitromuriatic acid do not touch it in the cold, except when they are very concentrated.

meline thus obtained is pure and finely divided, so that it may be perfectly washed, whilst it is impossible to wash the interior of the lumps obtained with too small a quantity of bichloride. The weight obtained then gives the quantity of sugar very exactly.—*Comptes Rendus*, August 28, 1854, p. 422.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Liverpool, September 20th, 1854.

On the Amounts of, and Methods of Estimating, Ammonia and Nitric Acid in Rain-water. By J. B. Lawes, Esq., F.R.S., *and* Dr. J. H. Gilbert, F C.S.

We were indebted to Cavendish for the observation, that ammonia and nitric acid were formed when humid air was submitted to voltaic action, about the commencement of the present century. De Saussure detected ammonia in the atmosphere; a few years later Chevreul observed its presence in the Seine; and in 1825 Brandes detected it in rain-water. Since that time much more minute attention has been paid to this subject, and also to the presence of *nitric acid* in meteoric and other waters. Liebig and Boussingault have particularly called attention to the influence which the ammonia carried down from the atmosphere must have upon the growth of plants; and the former of these philosophers pointed out the occurrence of nitric acid also in a considerable number of rain-waters which he examined, especially those of thunder-storms. Dr. H. Bence Jones has also found nitric acid in rain which fell in various parts of England and in the south of Ireland. But it is to the more recent labours of Boussingault that we are indebted for our most elaborate *quantitative* estimations of the *ammonia* in rain and other waters; and M. Barral has made a series of quantitative determinations of both the *nitric acid* and the *ammonia* contained in the rain-water which fell at Paris during several consecutive months in 1851.

It was chiefly with a view to the agricultural bearings of the subject, that the authors had entered upon the same field of investigation. But the object of the present paper was rather to discuss the methods of analysis, than to rely with confidence on the conclusions to which we might be led, by the more direct application of the results yet obtained, to the solution of the several important scientific and practical questions upon which they bore.

Tables were exhibited, showing the experimental results obtained in the estimation of ammonia in rain-water by several different methods.

In the first instance, very large amounts (from 100 to 200 lbs. or more) of rain-water, to which a little caustic potash was previously

added, had been distilled, and the distillation of the product repeated, collecting in each case about one-half the amount put into the retort, until the whole was reduced to a convenient bulk for further concentration in an open vessel. This was then evaporated, with a known amount of sulphuric acid, to a given volume; and measured portions of this final product were then neutralized by a standard alkaline solution, in the usual manner of liquid analysis. This method the authors conceived gave very good results; but it had been abandoned, from the great practical inconvenience, and frequent breakage, in conducting distillations in glass on so large a scale.

They had next adopted a method substantially the same as that of M. Boussingault, which was, to submit to a single distillation, generally not more than 1 litre (about 35 oz.) of water; two or more successive tenths or fifths of the product being then, with certain precautions, tested for ammonia by the liquid method. In this manner exceedingly minute *actual amounts* of ammonia could be determined; and in a careful and constantly practised hand, very valuable comparative results might be obtained. It happened however that, in relation to the *average total amount* of ammonia contained in a litre of rain or other waters, the minimum error was frequently not less, and sometimes considerably more, than 4 or 5 per cent. of such total amount.

The authors had therefore, in their more recent experiments, operated upon several litres of water in the first instance; reducing it by successive distillations to one-half, until thus brought to a convenient amount for final distillation, and subsequent testing of measured proportional amounts of the product, according to Boussingault's method. This modification, which the authors found M. Boussingault had himself suggested, but apparently not generally adopted, was considered to be important, and to be more applicable to this delicate subject of inquiry than either of the other methods which had been attempted.

However, some results obtained by the first method of large distillation, by the side of others of the same waters, by Boussingault's plan of small single distillations, showed considerable coincidence, such as to give confidence in the general principle of the methods.

The average of the determinations made on monthly mixed samples of the rain which fell at Rothamsted during more than a year, gave about 1 part of ammonia per million of rain-water; the average of many determinations made by Boussingault at Liebfrauenberg in Alsace was about four-fifths of this amount; whilst the estimations, both of M. Barral and M. Boussingault, at Paris gave as much as 3 or 4 parts, or even more, of ammonia per million of rain-water.

It was interesting too, to notice that the variations in the amount of ammonia which the authors had obtained, in the rain of different but entire months, when considered in connexion with the registered amounts of the fall, the direction of the wind, and the general characters of the weather, were perfectly consistent in kind with the

results of M. Boussingault in his special examinations of rain falling under different circumstances, of the water of dews, of fogs, &c.

The process adopted by the authors for determining the *nitric acid*, was to evaporate the rain-water with an alkaline carbonate several times to dryness, to weigh the solid residue, and determine its per-centage of nitrogen by Dumas' direct volume method of combustion with oxide of copper. With some of the results thus obtained however they were not satisfied; and they considered an accurate method for the determination of small quantities of nitrogen, or rather nitric acid, still a great desideratum. They hesitated therefore to apply with confidence all the results yet obtained to the discussion of the important questions with a view to the solution of which the investigation had been undertaken, and which they hope in future further to elucidate.

As a general result however it would seem, that whilst the per-centage amount of *ammonia* was generally less in the rain of thunder-storms and when there was a large fall of rain, the amount of *nitric acid*, on the other hand, appeared to be increased under the influence of storms. The results further indicated, that the amount of nitrogen yielded by rain-water *in the form of nitric acid* was considerably greater than that which existed *as ammonia*; and since there could be no doubt that nitrates applied as manures greatly enhanced the growth of plants by virtue of the nitrogen they contained, the amount of nitrogen brought down from the atmosphere in the form of nitric acid must be considered to have a very important influence on vegetation.—*Communicated by the Authors.*

On the Influence of the Solar Radiations on the Vital Powers of Plants, growing under different Atmospheric Conditions.—Part II*. *By* J. H. Gladstone, Ph.D., F.R.S.

The author, in continuing his account of experiments on this subject, described the effects produced on the prismatic spectrum by the different coloured glasses of which the bell-jars used in the investigation were made. The position of the rays cut off was determined by their relation to Frauenhofer's lines. Previous experiments on hyacinths were repeated, the bulbs being placed under colourless, blue, red, yellow, obscured colourless, and obscured yellow glasses, and in perfect darkness. The periods of growth of the several parts of the plant, under the different solar influences, were noted; and the general appearance was recorded. At the close of the experiment the increase in weight in each instance was calculated, and the lengths of the principal roots, leaves, and the flower-stalk were taken.

The detailed observations led to the following general conclusions:—Darkness promotes a rapid and abundant growth of thin rootlets; it prevents the formation of chlorophylle, but does not interfere much with the general healthiness of the plant, nor with the production of the colouring matter of the flowers. Partial obscurity

* An abstract of Part I. will be found in vol. x. p. 377.

produces the same effects in a modified manner, but greatly facilitates the absorption of water; and the cutting off of the chemical ray under such circumstances seems to make little difference. The withdrawal of all but the calorific rays interferes with the length of the roots, and produces a badly developed plant. The pure luminous ray causes the rootlets to be few and straggling, and diminishes the absorption of water. The hyacinths were well developed under the pure chemical influence.

Experiments were made on the germination, under like influences, of wheat and peas, as samples of the two great orders of plants. The first series was made in common air, the plants being placed on damp bricks, twelve seeds of each kind being employed in each separate instance. The periods of germination, and all the circumstances that marked the growth of the plants, were carefully noted; drawings were made, and at the close of the experiment, the height of the plants, the length of their roots, their weight, and the number of seeds that had germinated, were recorded. The effect of the same solar radiations on the two plants was extremely different. In respect to the wheat, it was found that, under the given circumstances, the absence of the chemical rays favours the first growth, and the presence of the luminous rays does not impede it. Afterwards the opposite effect takes place; the roots are retarded in their development by the yellow ray, much more than by all the rays of the spectrum in combination. The calorific ray is on the whole the most favourable to their growth, even more so than the complete absence of all solar radiations. The shooting forth of the plume is favoured also by the withdrawal of the chemical rays, especially just at first; but the full and healthy development of leaves requires all the rays of the spectrum, the luminous being particularly necessary. In respect to peas under the given circumstances, it was found that the cutting off of the chemical rays favours the first germination of the seed; and this appears to be the principal, if not the only advantage of the darkness obtained by burying the seeds in the soil.

The development of roots requires also the absence of the chemical ray, but is rather favoured than otherwise by heat and luminosity. The first development of the plumule also proceeds best under the same circumstances. Yet these are not the conditions which produce a healthy plant; they cause too rapid and succulent a growth; when the plant is fairly established, those radiations which are comparatively speaking devoid of light, but replete with chemical power, seem the most suited to it. The points in common between the different actions of the solar radiations on wheat and on peas are, that in both cases the cutting off of the chemical ray facilitates the process of early germination, and that both in reference to the protrusion of the radicles and the evolution of the plume; obscurity causes an unnaturally tall growth, and poor development of leaves; and the yellow ray exerts a repellent influence upon the roots, giving the wheat a downwards, and the pea-roots a lateral impulse. A comparison of the results obtained by means of the

yellow, of the obscured colourless, and the obscured yellow glasses, showed that the yellow ray has a specific action in many respects, but not of the character which has sometimes been ascribed to it. The diversity of effect of the same ray upon the two plants was well exhibited by what took place under the colourless and red glasses. Under the former there grew a tall and vigorous crop of corn-plants, with a mere matting of stunted roots from the peas, while under the latter a thick crop of green and spreading plants arose from the germinating peas, but the wheat were few and straggling, and unhealthy in appearance.

Comments were then made upon various statements of other observers, and experiments by Dr. Draper and M. Senebier in the same direction were detailed. A narrative was then given of some observations by the author on the growth of the *Collinsia* and *Mignonette*, both sown in mould, and placed under the various solar influences above described.

The question of germination in different gases was then entered upon. Seeds of the wheat and the pea were placed in jars, containing respectively carbonic acid gas, hydrogen from which every trace of oxygen was removed by pyrogallate of potash, common air from which carbonic acid was removed by caustic alkali, and normal atmospheric air. These merely corroborated the opinion generally entertained, that oxygen is absolutely requisite for instituting the first change in the cotyledons of the seed. Peas and wheat were also grown in oxygen gas, under the colourless and coloured bell-jars. They grew, and appeared to flourish best under the chemical influences of the blue glass. The author concluded his Report with a series of inquiries, suggested by the investigation, and necessary to the full elucidation of the subject.—*Communicated by the Author.*

On the Production of Boracic Acid and Ammonia by Volcanic Action. By Mr. R. Warington.

The author stated, that in 1841 a friend had visited one of the Lipari islands called Vulcano, situated about twelve miles north of Sicily. The height of the mountain Vulcano is 2000 feet, and the depth of the crater 700 feet. The sides of this depression are covered in places with a white snow-like substance about 1 inch in thickness, beneath which is a fused lava, similar in appearance to the slag of a glasshouse. The boracic acid rises in vapour, and condenses on the surface of the ground or in crevices at the bottom of the crater, from which about 2000 tons are said to be annually removed. It occurs connected with sal-ammoniac, and the author considers that it exists originally beneath the surface as a nitride of boron. When steam is passed over this compound, at a moderate red heat, it is completely converted into boracic acid and ammonia, which are for the most part volatilized with the aqueous vapours. This theory of the formation of boracic acid was considered by the author substantiated by the analysis of the snow-like mass, which

still contained nitride of boron adhering to it.—*Communicated by the Author.*

On the Concentration of Alcohol in Sömmering's *Experiments.* *By* Prof. Graham.

The author stated, that when an open vessel is filled with a mixture of alcohol and water, and exposed to the air, the alcohol goes off first and leaves the water; but if, as in Sömmering's experiments, a bladder be completely filled with dilute alcohol, the liquid will decrease in bulk, and the water pass through the membrane, leaving a much larger per-centage of alcohol in the bladder. Dry membrane does not exhibit this phænomenon, for a jar, the mouth of which is covered with dry bladder, allows the alcohol to escape first. The author believed that liquids diffuse mechanically, by a kind of repulsive force of the same nature as that exhibited by gases. When common salt is added to water in a jar, membrane tied over it, and immersed in a vessel containing pure water, diffusion takes place in quantity which has a relation to the per-centage of salt dissolved. Alcohol however exhibits an anomaly in this respect, for the quantity of alcohol which diffused itself through the membrane when 5 per cent. of alcohol was present in the liquid, was not increased when the per-centage of alcohol was 10, 15 or 20. The phænomenon indicates a sifting or separating power to reside in membrane, and introduces a third element, in addition to diffusion and osmose, into the discussion of the permeability of membranous septa. The author believed that Sömmering's experiment was an instance of arrested diffusion where more than 5 per cent. of alcohol was present. The action has some resemblance to the separating and secreting power of cells in the living organism, and may prove of great physiological interest, particularly if the action should be found to extend to albumen, and other organic substances.—*Athenæum.*

On the Fluorescence exhibited by certain Iron and Platinum Salts. *By* Dr. Gladstone.

The peculiar blue appearance which presents itself on the surface of a solution of bisulphate of quinine, and some other substances, and which has received the name of "fluorescence," was noticed by the author in the red solution that results when a ferric salt in large excess is added to meconic acid; in the blue solution of ferrocyanide of iron dissolved in oxalic acid; in gallate of iron; and in the red solution formed when 2 equivs. of iodide of potassium are added to 1 of bichloride of platinum. Some observations were made on the composition of the salts in these solutions. In these iron salts the blue appearance was found not to be produced by extra-spectral rays, as observed by Stokes in the bisulphate of quinine; but by rays which coincided to a certain extent with the ordinary blue ray, when a prismatic spectrum was thrown on to a vessel filled with the solution.—*Athenæum.*

THE CHEMICAL GAZETTE.

No. CCXC.—November 15, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the so-called Benzoic Oxide. *By* Drs. LIST *and* LIMPRICHT.

THE authors have examined the products of the distillation of benzoate of copper, and amongst these especially the benzoic oxide discovered by Ettling and Stenhouse*.

From this investigation, it appears that the benzoic oxide is benzoate of oxide of phenyle, and that this is identical with the benzophenide, obtained by Gerhardt and Laurent by the treatment of carbolic acid with chloride of benzoyle. Together with this body, the distillate contains benzine, benzoic acid and two oleaginous bodies. The gases evolved were not examined.

The authors distilled the dry benzoate of copper upon the open fire until no more vapours were evolved. Ettling only heated it to 527° F., and then found salicylous acid in the residue; the authors consequently obtained at a higher temperature products of the distillation of the first-formed salicylite of copper.

The butyraceous distillate is saturated with carbonate of soda to fix the acids, and then distilled with water, when nearly pure benzine, $C^{12}H^6$, passes over. The residue is treated with water, and the benzoate of soda washed out; the residue then left is dissolved in hot alcohol, and set to crystallize. By treating the brown crystals with a little alcohol, brown oleaginous substances are separated from the benzoic oxide, which now crystallizes in a pure state. The oleaginous bodies will be mentioned hereafter.

The substance is obtained in particularly beautiful crystals from a mixture of æther and alcohol; its analysis and properties prove it to be nothing but

Benzoate of Oxide of Phenyle, $C^{12}H^5O, C^{14}H^5O^3$.—The analysis did not lead to the formula $C^{14}H^5O^2$, but to the proportions $C^{13}H^5O^2$. The crystals are rhombic prisms. The analyses gave:—

Carbon	78·67	78·13	77·84	13	= 78	78·78
Hydrogen	5·06	5·08	5·00	5	5	5·09
Oxygen.....	..	..	..	2	16	16·23

Decomposition of Benzoate of Oxide of Phenyle.

1. In contradiction to the statements of Stenhouse and Ettling, benzoic oxide may be boiled with a watery solution of potash without undergoing any decomposition. When heated in closed tubes to 302° to 338° F., it dissolves completely in hydrated potash. On

* Phil. Mag., July 1845.

opening the tubes, no gas (hydrogen) escapes; the products which separate on the neutralization of the potash by means of sulphuric acid are benzoic and carbolic acids. The same decomposition is produced by heating with an alcoholic solution of potash.

2. The alcoholic solution of benzoate of oxide of phenyle may be evaporated with ammonia at boiling-heat without any decomposition. Heated to 302° F. in closed tubes, it furnishes carbolic acid and benzamide. Heated in a current of dry ammonia, benzoic oxide also furnishes benzamide and carbolic acid, but no aniline.

3. Benzoate of oxide of phenyle is not attacked by acids such as phosphoric and oxalic acids; it dissolves in sulphuric acid. Water precipitates benzoic acid from this solution, and the solution contains sulphocarbolic acid.

Derivatives of Benzoate of Oxide of Phenyle.—Fluid bromine acts upon benzoate of oxide of phenyle at ordinary temperatures; hydrobromic acid is formed, together with a solid body, which, after recrystallization from alcohol, forms long white needles. The mother-liquor of these crystals still contained an oleaginous body, which is soluble in æther, and crystallizes from this solution in small white crystals. This last body could not be further investigated.

The substance crystallizing in long needles dissolves readily in æther and hot alcohol; it is insoluble in water, fuses below 212° F., and sublimes without decomposition. It consists of a mixture of two compounds; both are benzoate of oxide of phenyle, but in one of them 1, in the other 2 atoms of the hydrogen of the oxide of phenyle has been displaced by bromine. The oleaginous body above described is perhaps also a similar product of substitution containing 3 atoms of bromine. The composition of these three compounds must be as follows:—

I. $C^{26}\left\{\begin{matrix}H^9\\Br\end{matrix}\right.O^4$.			II. $C^{26}\left\{\begin{matrix}H^8\\Br^2\end{matrix}\right.O^4$.			III. $C^{26}\left\{\begin{matrix}H^7\\Br^3\end{matrix}\right.O^4$.		
C^{26}	156	56·31	C^{26}	156	43·82	C^{26}	156	35·86
H^9	9	3·25	H^8	8	2·25	H^7	7	1·61
Br	80	28·88	Br^2	160	44·94	Br^3	240	55·17
O^4	32	21·56	O^4	32	8·99	O^4	32	7·36

Their analyses gave,—

C	55·95	54·97	50·11	46·55	43·15	42·74			
H	3·88	3·19	2·93	2·46	2·59	2·04			
Br	..	..	34·65	..	..	45·42	32·48	37·69	42·82

The formulæ of the two bodies produced are,—

$$C^{14}H^5O^3, C^{12}\left\{\begin{matrix}H^4\\Br\end{matrix}\right.O^4 \quad \text{and} \quad C^{14}H^5O^3, C^{12}\left\{\begin{matrix}H^3\\Br^2\end{matrix}\right.O^4.$$

Alcoholic solution of potash and sulphuric acid separate benzoic acid from these bodies, in accordance with the formulæ. After the neutralization of the first with sulphuric acid, the benzoic acid is obtained together with an oil, which must be a mixture of mono-

bromocarbolic acid and bibromocarbolic acid. The authors are consequently of opinion, that the body obtained by Stenhouse by treating benzoic oxide with chlorine, which, after repeated crystallization from alcohol, consisted of flat four-sided prisms, fusing at 188° F., is a mixture of two products of substitution, of similar composition to the bromine compounds above described. Stenhouse's analyses justify this opinion. Moreover, Stenhouse resolved his chlorinated substance, by treatment with alcoholic solution of potash, into benzoic acid free from chlorine, and a resin smelling like creosote, which must consequently have consisted of a mixture of monochlorocarbolic acid, $C^{12}(H^5Cl)O^2$, and bichlorocarbolic acid, $C^{12}(H^4Cl^2)O^2$.

Nitrobenzoate of Oxide of Binitrophenyle, $C^{14}(H^4NO^4)O^3 + C^{12}H^3(2NO^4)O$.—Nitrosulphuric acid (1 part of nitric and 2 of sulphuric acid) converts the benzoate of oxide of phenyle into one, or perhaps two nitride compounds, in which hydrogen is displaced by NO^4, not only in the oxide of phenyle, but also in the benzoic acid. This body is insoluble in cold water and alcohol, difficult of solution in æther and boiling alcohol, and crystallizes from its solution; when sufficiently purified, it is white, fuses at 302° F., remains amorphous and transparent on cooling, and only becomes crystalline when touched with some sharp object. It fuses when heated upon platinum foil, and burns with a smoky flame; when heated in a tube, it produces a slight explosion. Alcoholic solution of potash decomposes this compound; the products are nitrobenzoate of potash and binitrocarbolate of potash, the latter crystallizing in beautiful golden-yellow needles. The substance also undergoes the same decomposition when treated with sulphuric acid at a gentle heat. The products of the treatment of nitrobenzoate of oxide of binitrophenyle will be further studied by the authors. The following analysis of the nitrobenzoate differs a little from the calculated results, whence the authors conclude that a little of a second compound, perhaps $C^{26}(H^8 2NO^4)O^4$, was mixed with it. The substance, dried at 212° F., gave,—

Carbon.....	47·72	47·50	26 =	156	46·84
Hydrogen	2·79	2·56	7	7	2·10
Nitrogen	..	..	3	42	12·61
Oxygen	..	..	16	128	38·45

Nitrobenzoate of Oxide of Bibromophenyle, $C^{14}(H^4NO^4)O^3 + C^{12}(H^3Br^2)O$, is obtained by treating the above-described benzoate of oxide of bibromophenyle with nitrosulphuric acid. In its physical properties it resembles the preceding nitride compound. It fuses between 194° and 212° F., and is resolved, by treatment with alcoholic solution of potash, into nitrobenzoic and bibromocarbolic acids. Analysis:—

Carbon.....	40·41	26 =	156	38·90
Hydrogen.....	2·04	7	7	1·74
Bromine	41·16	2	160	39·90
Nitrogen	..	1	14	3·49
Oxygen	..	8	64	15·97

The authors give the following tabular view of the known compounds of benzoic acid with oxide of phenyle and their derivatives:—

Benzoate of oxide of phenyle	$C^{14} H^5 O^3, C^{12} H^5 O.$
Benzoate of oxide of monochlorophenyle	$C^{14} H^5 O^3, C^{12} \left\{ \begin{matrix} H^4 \\ Cl \end{matrix} \right. O.$ (Stenhouse.)
Benzoate of oxide of monobromophenyle	$C^{14} H^5 O^3, C^{12} \left\{ \begin{matrix} H^4 \\ Br \end{matrix} \right. O.$
Benzoate of oxide of bibromophenyle	$C^{14} H^5 O^3, C^{12} \left\{ \begin{matrix} H^3 \\ Br^2 \end{matrix} \right. O.$
Benzoate of oxide of binitrophenyle	$C^{14} H^5 O^3, C^{12} \left\{ \begin{matrix} H^3 \\ 2NO^4 \end{matrix} \right. O.$ (Gerhardt & Laurent.)
Benzoate of oxide of trinitrophenyle	$C^{14} H^5 O^3, C^{12} \left\{ \begin{matrix} H^2 \\ 3NO^4 \end{matrix} \right. O.$ (Gerhardt & Laurent.)
Nitrobenzoate of oxide of binitrophenyle	$C^{14} \left\{ \begin{matrix} H^4 \\ NO^4 \end{matrix} \right. O^3, C^{12} \left\{ \begin{matrix} H^3 \\ 2NO^4 \end{matrix} \right. O.$
Nitrobenzoate of oxide of bibromophenyle	$C^{14} \left\{ \begin{matrix} H^4 \\ NO^4 \end{matrix} \right. O^3, C^{12} \left\{ \begin{matrix} H^3 \\ Br^2 \end{matrix} \right. O.$

The remarkable circumstance, that benzoate of oxide of phenyle, which is so easily decomposed by concentrated sulphuric acid, undergoes no decomposition by treatment with a mixture of nitric and sulphuric acids, led the authors to make an experiment with benzoate of oxide of æthyle, which was actually converted into nitrobenzoic æther. The nitride compounds of many compound æthers may therefore certainly be obtained in this manner.

As regards the preparation of benzoate of oxide of phenyle, it is most readily procured by distilling anhydrous benzosalicylous acid, as stated by Gerhardt, instead of benzoate of copper, from which only a proportionably small result is obtained. The benzosalicylous acid appears to be directly decomposed by heat into carbonic acid and benzoate of oxide of phenyle. The distillate, even to the last drops, when dissolved in alcohol, furnishes nearly pure crystals of the new body. On the other hand, a mixture of equivalents of anhydrous benzoic and salicylous acids furnished no benzoate of oxide of phenyle on distillation. Neither the treatment of carbolic acid with chloride of benzoyle, nor the distillation of benzoate of soda with sulphocarbolate of lime, furnished any of this product.

It has been stated above, that in the preparation of benzoate of oxide of phenyle by the distillation of benzoate of copper, the crystals of the principal product must be separated from a brown oleaginous body. The authors purified this oil by repeated fractional distillation. The purified oil, when distilled at 392° F., furnished pure carbolic acid. At 500° F. a colourless oil, of an unpleasant geranium-like odour, passed over; it is insoluble in water, dissolves with difficulty in alcohol, but readily in æther. It burns in the air

with a pale luminous flame. According to the following analyses, it has the composition $C^{22} H^9 O^2$:—

Carbon.....	84·35	84·60	22 =	132	84·07
Hydrogen	5·99	5·93	9	9	5·73
Oxygen	..	..	2	16	10·20

This oil is not changed by alcoholic solution of potash; when heated with concentrated sulphuric acid, and afterwards diluted with water, it furnishes a crystalline hydrocarbon isomeric with naphthaline, $C^{10} H^4$, whilst carbolic acid remains in the acid fluid. The crystalline body, which is perhaps identical with the hydrocarbon obtained by Chancel by the distillation of benzoate of lime, gave on analysis,—

Carbon	83·41	10 = 60	93·75
Hydrogen	6·66	4 4	6·25

Judging from these products of decomposition, the oil which boils at 500° F. is perhaps a compound of the formula $C^{12}(H^5 C^{10} H^4)O^2$, like carbolic acid, in which 1 equiv. of hydrogen has been displaced by the hydrocarbon $C^{10} H^4$.

At the conclusion of their memoir, the authors express the very probable opinion, that a great number of known bodies may have a constitution analogous to that of the compound æthers. Thus Ettling's parasalicyle, which was obtained by the distillation of salicylite of copper, is perhaps nothing but benzoate of salicylous acid, $C^{28} H^{10} O^6$, obtained by Cahours by the treatment of salicylous acid with chloride of benzoyle.

Instead of regarding oil of bitter almonds as the aldehyde of benzoic acid, the authors represent it by doubling the formula, as $C^{14} H^5 O^3 + C^{14} H^7 O$, according to which it is a compound of benzoic acid with the oxide of the alcohol of benzoic acid.

Oil of cummin, $C^{20} H^{12} O^2$, may be represented in a similar manner as $C^{20} H^{11} O^3 + C^{20} H^{13} O$, and perhaps the oxide of cinnamyle contained in oil of cinnamon, $2(C^{18} H^6 O^2) = C^{18} H^7 O^3 + C^{18} H^9 O$. Thus oxide of cinnamyle would be isomeric with styracine, which has already been recognized to be a combination of cinnamic acid with the oxide of its alcohol.—Liebig's *Annalen*, xc. p. 190.

On Æsculetine and Oil of Marjoram. By Dr. F. Rochleder.

In his investigation of the action of the alkaline sulphites upon organic substances, the author has also tested the deportment of æsculetine and oil of marjoram.

Oil of marjoram, when heated with a concentrated solution of bisulphite of ammonia or soda, separates into a fluid portion and a solid white mass. It is immaterial whether the salt of ammonia or soda be employed; the products remain the same. The fluid portion is mechanically separated from the solid product; the latter is triturated, and washed with alcohol, æther and water. It forms an amorphous white powder. It neither contains sulphur, nor soda, nor ammonia. It consists of carbon, hydrogen and oxygen.

The author will give his analyses hereafter. The fluid portion of the oil of marjoram is purified by distillation with water, by which it is obtained free from colour. This oil belongs to the class of camphenes.

Æsculetine readily dissolves in a concentrated watery solution of bisulphite of ammonia at a boiling heat. If the boiling be continued for a short time, no trace of the sparingly soluble æsculetine separates. The yellowish solution, after the addition of alkalies, attracts oxygen with great avidity. A few drops of ammonia produce a darker yellow colour, and the solution, when agitated with air, immediately passes to a blood-red; it finally becomes of a deep indigo-blue colour. If, instead of ammonia, solution of hydrate of baryta be carefully added to the solution, the sulphurous acid of the excess of bisulphite of ammonia is thrown down in the form of sulphite of baryta. As soon as the excess of sulphurous acid is removed, the fluid becomes blood-red by the absorbtion of oxygen. The substance produced from æsculetine by bisulphite of ammonia has not yet been separated from that salt; but, on the other hand, the product of the oxidation of this body has been obtained. If a solution, which has become blue by the addition of ammonia and shaking with air, be mixed with salts of lead or baryta, a dark violet or dark indigo-blue precipitate is produced, according as the fluids are somewhat acidulated or neutral. If the indigo-blue lead salt be stirred with water and decomposed by sulphuretted hydrogen, a beautiful green solution is produced, which, when mixed with a little water, loses the green colour, and becomes nearly colourless, with a yellowish tinge. Concentration reproduces the green colour. The green fluid, when left standing for some days in the air, becomes of a beautiful blood-red colour. The residue left by the green fluid is of a dark blackish-green, and dissolves again with a green colour; the red fluid leaves a dark residue, like carthamine. The red substance gives blue salts with bases. By dry distillation, an orange-yellow colouring matter is produced, together with a large quantity of a white ammoniacal salt, which, when heated with muriatic acid, deposits much sulphur, whilst muriate of ammonia is formed and sulphurous acid evolved. Another body is also contained amongst the products of distillation, which is readily converted into green and red products by reagents. If the solution of æsculetine in boiling bisulphite of ammonia be mixed with as much baryta-water as is necessary to remove the free sulphurous acid, filtered from the sulphite of baryta, and the filtrate heated upon the water-bath, a dark red fluid is obtained; this is of a dark cherry-red colour by transmitted, and of a beautiful blood-red by reflected light. When diluted with a large quantity of water, the fluid becomes pale yellowish by transmitted light, but still remains intense blood-red by reflected light. This red fluid, when saturated with carbonic acid, becomes dark, but reacquires its pale red colour when the carbonic acid is expelled. All the substances mentioned contain carbon, hydrogen, oxygen, nitrogen and sulphur. The presence of sulphur is only to be recognized after the destruction of the substance.

Boiling with muriatic acid evolves neither sulphuretted hydrogen nor sulphurous acid. The nitrogen also is not contained in these compounds in the form of ammonia. The author will hereafter communicate his views upon the differences which occur in the comparison of his previous memoirs and that of Zwenger with regard to æsculine.—*Sitzungsber. der Akad. der Wiss. zu Wien, Math. Naturw. Cl.*, xiii. p. 169.

On Oxychloride of Phosphorus. By Dr. W. Casselmann.

In the progress of some investigations upon the so-called oxychlorides, I have observed that oxychloride of phosphorus enters into a well-characterized combination with perchloride of tin. It is produced immediately in the form of a white crystalline mass when the two fluids are mixed in proper proportions, and when one of the latter is present in great excess, the compound shoots into separate large crystals. It has a peculiar odour, and fuses at 131° F. into a clear colourless fluid, which, when heated far above its melting-point, may remain fluid for several days at the ordinary temperature of a room, and then suddenly solidify. A freezing mixture of snow and salt produces solidification immediately. At 356° F. the fluid boils, and when carefully protected from the access of moist air, distils over completely and without change. When exposed to the air, it fumes, attracts water, forming in the first place crystals of hydrated perchloride of tin, and then deliquescing into a solution of perchloride of tin, muriatic acid and phosphoric acid; a larger quantity of water produces a precipitate of phosphate of tin. Analyses gave the formula $2SnCl^2+PO^2Cl^3$ for its constitution.

If oxychloride of phosphorus be mixed with the compound $SnCl^2+2SCl^2$ in closed vessels, the whole dissolves into a yellow fluid, from which the above-mentioned compound crystallizes after some time. A yellow fluid remains on the crystals, and this is probably bichloride of sulphur. As soon as the vessels are opened, however, chlorine escapes, and the yellow fluid then deposits sulphur on solution in water, a proof that it has become a lower chlorine compound.

The described properties of the substance above mentioned, especially its behaviour at a high temperature, exclude the supposition that it contains any ready-formed phosphate of tin; and for this reason it will be impossible to adopt Berzelius's views of the constitution of the oxychlorides for oxychloride of phosphorus (according to him it would be a compound of phosphoric acid with pentachloride of phosphorus). On the contrary, in its combining properties it exhibits exactly the character of an electro-negative chloride. From this some support might be derived for Gerhardt's view*, according to which it is to be regarded as a chloride of the radical PO^2, phosphoryle. The consequences of this hypothesis would lead to the adoption of radicals CrO^2, chromyle; SO^2, sulphuryle, &c.; and the latter would then present an instance of one and the same substance being capable of acting at once as an oxyacid and as a

* Liebig's Annalen, lxxxvii. p. 57.

radical, a view which, according to the ideas at present received of the oxyacids, could hardly be adopted without a complete revision of the whole system of chemistry.

This is certainly a sufficient reason for receiving such theories with great caution, and only after their validity has been tested in the greatest possible number of different cases.

If the formula above given ($2SnCl^2 + PO^2Cl^3$) be compared with that of a body described by me two years ago*, $2SnCl^2 + PCl^5$, their mutual resemblance will immediately show the possibility of regarding oxychloride of phosphorus as $P\left\{\begin{matrix}O^2\\Cl^3\end{matrix}\right\}$, *i. e.* as a substance which contains phosphorus as a radical, and which has been produced from the pentachloride of phosphorus by the displacement of Cl^2 by O^2, in such a manner that the character of the original chloride, as far as is indicated by its combining proportions, has remained unchanged.—Liebig's *Annalen*, xci. p. 241.

On Quercitrine. *By* M. Rigaud.

The author has investigated the colouring matter of quercitron bark in Will's laboratory. The colouring matter contained in it, called quercitrine by Chevreul, has since been investigated by Bolley, who called it quercitric acid; and his investigation shows it to be probable that this body contains sugar, and therefore belongs to the glycosides, as he found that it furnished formic acid by treatment with oxidizing agents.

Rigaud's quercitrine, $C^{36}H^{20}O^{21}$, or more probably $C^{36}H^{19}O^{21}$, was prepared essentially according to Bolley's directions. The commercial bark was extracted with alcohol of spec. grav. 0·849; the expressed fluid was freed from quercitron-tannic acid and a brown body by gelatine or animal membrane. This purified solution was further evaporated after the distillation of the alcohol, replacing the alcohol as it evaporated by water, when the quercitrine, which is insoluble in hot water, is deposited. By the direct evaporation of the alcoholic solution, only a brown extract is obtained. The substance is obtained pure by repeated solution in alcohol, and separation by means of water.

It is of a sulphur or chrome-yellow colour, of a slightly bitter taste, inodorous, composed of microscopic crystals of the right-rhombic system, which do not polarize light; it is soluble in 425 parts of boiling water (400 parts according to Bolley), is readily soluble in dilute ammonia and solution of soda, sparingly soluble in æther, and almost insoluble in cold water. The ammoniacal solutions become darker in the air, and acquire at last a dark brown colour. In dry distillation, it fuses, becomes darker in colour, and for the most part decomposed; the residue is a light cinder, whilst the receiver contains a small quantity of a sublimate accompanied by the ordinary products of dry distillation, such as empyreumatic oils. Both the aqueous and alcoholic solutions of quercitrine give a dark

* Liebig's Annalen, lxxxiii. p. 257.

green colour with perchloride of iron, without producing a precipitate; the colour is still observable when the solution is diluted 4000 to 5000 times. Its analysis gave,—

				Bolley.		
Carbon ..	53·04	53·07	53·66	52·486	36	53·59
Hydrogen	5·03	4·91	5·22	4·958	19	4·71
Oxygen ..	41·93	41·62	41·12	42·556	21	41·70

The analyses differ principally in the amount of carbon from Bolley's, who calculated for this body the formula $C^{16} H^{9} O^{10}$. The author founds his proposed formula upon the following facts.

Quercetine, $C^{24} H^{10} O^{11}$.—If quercitrine be boiled with much water and dilute sulphuric acid, a substance of a brighter colour separates, and a kind of sugar is contained in the fluid. The author calls this yellow body quercetine. When pure, it is a citron-yellow powder, with a greenish tint; and when examined under the microscope, it is found to consist of transparent crystalline needles, which do not polarize light. It is tasteless and inodorous, and undergoes no change in the air. It is but sparingly soluble in hot water, but dissolves readily in alcohol. It is soluble in acetic acid when hot, but separates for the most part on cooling. It possesses the character of a weak acid. Water containing a little potash or soda dissolves it with the greatest facility, and with a golden-yellow colour. On the addition of an acid, it separates again in flakes, whilst the colour disappears. It is also readily soluble in ammonia; the solution constantly becomes darker when exposed to the air, until at length it acquires a humus-like colour. When heated upon platinum foil, it fuses, and burns with a strongly fuliginous flame, leaving a light coal as a residue, which disappears entirely at a more intense heat.

The solution of quercetine gives the same green colour with perchloride of iron as that of quercitrine, a property possessed by these bodies in common with æsculine and æsculetine. Quantitative determinations of the sugar (by Fehling's method) gave 44·35 per cent. of sugar, supposing it to be grape-sugar. The quercetine being nearly insoluble in water, could also be determined directly by collecting and weighing. From 100 parts of quercitrine the author obtained 61·44 of quercetine. From this he calculated the following formula for quercitrine, $C^{36} H^{20} O^{21}$; during decomposition an equivalent of grape-sugar would be produced by the assimilation of 2HO, leaving for quercetine $C^{24} H^{10} O^{11}$; thus—

$$\underset{\text{Quercitrine.}}{C^{36} H^{20} O^{21}} + 2HO = \underset{\text{Grape-sugar.}}{C^{12} H^{12} O^{12}} + \underset{\text{Quercetine.}}{C^{24} H^{10} O^{11}},$$

of which the per-centage composition agrees with that found by analysis:—

Carbon	59·15	59·05	59·26	59·48
Hydrogen	4·05	4·35	4·27	3·84
Oxygen	36·80	36·60	36·47	36·68

The author nevertheless considers it to be more probable that the formula of quercitrine is $C^{36} H^{19} O^{21}$, which would consequently, by

the reception of 2HO and the elimination of $C^{12}H^{10}O^{10}$, give $C^{24}H^{9}O^{11}$ for quercetine. The decomposition would therefore be represented in the following manner:—

$$C^{36}H^{19}O^{21} + 2HO = C^{12}H^{12}O^{12} + C^{24}H^{9}O^{11}.$$

Quercitrine. Grape-sugar. Quercetine.

The sugar formed by the splitting of the quercitrine does not deviate the plane of polarization. From the analyses it appears to have the composition $C^{12}H^{15}O^{15}$ or $C^{12}H^{12}O^{12} + 3HO$. It tastes much sweeter than grape-sugar.—Liebig's *Annalen*, xc. p. 283.

On Panaquilone, a new Vegetable Matter. *By* S. GARRIGUES.

The author has investigated ginseng root. It is a highly esteemed drug in China, and is obtained from a species of *Panax*. Its occurrence in Canada was made known by Sarrasin in 1703; the root is there called *Osteeraagweh*. The Canadian root is obtained from *Panax quinquefolius*. It varies from the thickness of a quill to that of a finger, is a few inches long, of a brownish-yellow colour and generally finely annulated externally, yellowish-white and spongy internally. When fresh, it has an aromatic odour, which becomes weak by drying; its taste resembles that of liquorice root, but leaves an unpleasant bitter taste behind it. It was first chemically examined by Rafinesque, who stated that the root contained a camphor-like substance.

The author has found a new body in this root, to which its taste, and perhaps also its efficacy, are due. It is prepared from the syrupous infusion, obtained according to Wöhler's recipe by displacement, by the addition of a saturated solution of sulphate of soda. This produces a thick, sticky, brown precipitate, which is washed with a solution of the same salt, and then treated with absolute alcohol, which dissolves the new body, leaving the salt as a residue. The substance left after the distillation of the alcohol was dissolved in water, the solution treated with animal charcoal, again evaporated, and the mass obtained redissolved in absolute alcohol. The body thus obtained is called by the author

Panaquilone.—It has the composition $C^{24}H^{25}O^{18}$; it is an amorphous yellow powder, readily soluble in water and alcohol, and insoluble in æther. It has a taste like glycyrrhizine, but rather bitter. When heated, it fuses, with decomposition. It burns without residue. Its solution gives no precipitate either with acids or with chloride of mercury or platinum, but tannic acid produces a precipitate. It acquires a brown colour with alkalies. When heated with hydrate of potash, panaquilone furnishes no ammonia. Acids convert panaquilone into a white substance, insoluble in water, which the author names *panacone*; carbonic acid and water are separated. Panaquilone is dissolved by concentrated sulphuric acid with a purple-red colour. If this solution be poured into water, a white precipitate of panacone is produced. No sugar is separated in this rocess. When muriatic acid, or what is better nitric acid, is added

to a concentrated solution of panaquilone, and the whole is gently heated, the panacone separates immediately in the form of a white powder, with a slight evolution of carbonic acid; when the heat is increased, it fuses beneath the fluid.

Analyses of panaquilone gave,—

Carbon	45·43	45·97	45·91	24	46·00
Hydrogen.....	8·20	8·05	8·05	25	7·98
Oxygen.....	46·37	45·98	46·04	18	46·02

Panacone has the composition $C^{22} H^{19} O^8$; it is a powder which appears crystalline under the microscope; tasteless and insoluble in water and æther. It dissolves in alcohol. It dissolves with a purple colour in concentrated sulphuric acid, and is thrown down again from this solution by water as a white powder. With hot concentrated nitric acid it furnishes oxalic acid. Alkalies have no action upon it. It is very fusible and burns with flame without leaving any residue. Its analyses gave,—

Carbon.....	59·218	61·06	22	61·43
Hydrogen	8·934	8·85	19	8·83
Oxygen	31·848	30·09	8	29·74

Liebig's *Annalen*, xc. p. 231.

On the Action of Hydriodic Acid upon Glycerine.
By MM. Berthelot *and* de Luca.

Glycerine, saturated with hydriodic acid gas, and kept for fourteen hours in a closed vessel at 212° F., and then treated with potash and æther, furnishes a peculiar iodized liquid, *iodhydrine*.

It is a syrupous liquid, of a golden colour, dissolving one-fifth of its volume of water, but insoluble in water; it is soluble in alcohol, and has a saccharine taste; it is not volatile, but burns without residue, evolving vapours of iodine. Its density is 1·783.

Its analysis gave nearly constant numbers with different preparations. These numbers may be represented by the formula $C^{12} H^{11} IO^6$:—

$$2C^6 H^3 O^6 + HI = C^{12} H^{11} IO^6 + 6HO.$$

Treated with potash at 212° F., iodhydrine is very slowly decomposed. It furnishes by this means a substance analogous to, or identical with glycerine, and iodide of potassium, together with a tolerably volatile liquid, free from iodine, which is soluble in æther. An analysis of this product gave numbers corresponding with the formula $C^6 H^5 O^3$:—

$$C^6 H^3 O^6 = C^6 H^5 O^3 + 3HO.$$

It is possible that the iodine contained in cod-liver oil and the analogous oils may exist in the form of iodhydrine, or some similar compound.—*Comptes Rendus*, October 16, 1854, p. 748.

On Cuminic Alcohol. By M. Kraut.

The author has treated oil of cummin with a solution of potash in alcohol, and resolved it in this manner into cuminic acid and its alcohol.—Liebig's *Annalen*, xc. p. 384.

ANALYTICAL CHEMISTRY.

On the Estimation of Free Bromine in presence of Hydrobromic and Hydrochloric Acids. By C. Greville Williams*.

In studying the action of bromine on oil of turpentine, I ascertained that by causing the reaction to take place in presence of water, 1 equiv. of turpentine was capable of decolorizing 1 equiv. of bromine. The transition of colour was so perfectly marked, that I proposed to found upon it a process for estimating the equivalents of some hydrocarbons, more especially those of the terebric class†; and in another research I endeavoured to explain more fully than in the first memoir, the nature of the somewhat complex decomposition which takes place, and supported the view which I took of its nature by analysis of the bromide of turpentine, and estimations of the amount of hydrobromic acid formed during the reaction‡.

Knop§ has taken exception to my method of performing the operation, while admitting the principle, and published a lengthy memoir on the subject, the experiments in which were worked out by an elaborate modification of my process.

His chief objections appear to be, that the repeated addition of volatile substances by small portions involved a certain loss of material, and that as the ingredients were added in an undiluted form, any error of manipulation had an important bearing upon the equivalent sought to be educed. He obviates this by diluting the hydrocarbon by certain liquids having little tendency to react upon bromine, and uses the volumetrical method of estimation; he also makes several other modifications in the various manipulations.

With regard to the dilution of the hydrocarbon, I had already made several experiments with alcoholic solutions containing known per-centages of various oils, and I adopted this method more especially in the converse operation to that described in my former memoir, namely, the estimation of free bromine; the process moreover afforded me unexceptionable results under circumstances which, it is believed, had until then remained an unsolved problem. In fact, my more recent experiments show that free bromine may be estimated with equal precision, and much greater rapidity, by means of an alcoholic solution of turpentine than the usual quantitative

* Communicated by the Author.

† "On a Method of ascertaining the Equivalents of some Fluid Hydrocarbons by means of Bromine," Chem. Gaz., October 1, 1853.

‡ Chemist, November 1853. § Central Blatt for May 3, 1854.

method as bromide of silver, and that the presence of hydrochloric or hydrobromic acid has no injurious effect upon the result.

The experiments were made with bromine-water, and also with aqueous solutions of that element containing large quantities of hydrochloric and hydrobromic acids.

To perform the operation, it is essential, in the first place, to prepare a pure oil of turpentine, which is easily done by dehydrating with chloride of calcium, and rectifying until a correct boiling-point is obtained.

To make the standard solution, it is only necessary to add 10 parts by weight of the purified oil to 90 parts of alcohol.

The standard solution may be added by small portions from a Schuster's alkalimeter, the liquid holding the free bromine in solution being contained in a stoppered bottle, which at every addition must be violently agitated; as the turpentine increases in quantity, the colour gradually disappears, and at last the contents of the bottle become quite colourless; the operation being then concluded, the alkalimeter may be reweighed, and as 10 parts of the liquid added contain only 1 part of turpentine ($C^5 H^4$), every 340 parts of the standard solution indicate 80, or 1 equiv. of bromine.

The following experiments were made to test the accuracy of the process.

Quantity of bromine used in each experiment 47·7 cub. centims.

Turpentine Process.

	Turpentine used.	Bromine indicated.
I.	1·77	4·16
II.	1·77	4·16
III.	1·85	4·35
IV.	1·85	4·35
V.	1·80	4·23
VI.	1·80	4·23
VII.	1·77	4·16
VIII.	1·77	4·16

Mean of eight turpentine estimations. 4·225

Silver Process.

	AgBr obtained.	Br indicated.
I.	9·75	4·15
II.	9·76	4·15
III.	9·75	4·15
IV.	10·02	4·26
V.	10·12	4·30
VI.	10·23	4·35

The first two estimations were made by converting the bromine into bromide of potassium, heating to redness, and, after rendering slightly acid, precipitating with nitrate of silver; the four last by saturating the bromine with pure ammonia, then adding dilute nitric acid in slight excess and precipitating as before.

Mean of six silver determinations. 4·226

47·7 cub. centims. of bromine-water of a different preparation:—

Turpentine Experiments.

	Turpentine used.	Br indicated.
I.	4·12	9·69
II.	4·05	9·53

Mean of two turpentine determinations. 9·61

Silver Experiments.

	BrAg obtained.	Br indicated.
I.	22·02	9·37
II.	22·42	9·54
III.	22·44	9·54

Mean of three silver determinations. 9·48

Estimation of Bromine in presence of Hydrobromic Acid.

47·7 cub. centims. bromine-water, the same as used in the last experiment, mixed with half its bulk of moderately strong hydrobromic acid:—

	Turpentine used.	Bromine indicated.
I.	4·05	9·53
II.	3·92	9·22

Mean of two turpentine determinations.	Mean of three silver determinations before addition of hydrobromic acid.
9·375	9·480

If we compare the two experiments in which the hydrobromic acid was present with the mean of the silver determinations of the same bromine made previously to the addition of the hydrobromic acid, we find a remarkably close approximation in the numbers.

It is seen therefore that the turpentine process enables us to determine free bromine with accuracy in presence of hydrobromic acid.

Estimation of Free Bromine in presence of strong Hydrochloric Acid.

47·7 cub. centims. bromine-water, same as the last, mixed with half its bulk of strongest hydrochloric acid:—

	Turpentine used.	Bromine indicated.
I.	4·20	9·88
II.	4·12	9·69

Mean of two turpentine determinations in presence of strong hydrochloric acid.	Mean of silver determinations previous to addition of hydrochloric acid.
9·78	9·48

The last experiments show that hydrochloric acid, although it appears to have a slightly retarding effect upon the reaction, does not interfere sufficiently to lessen the value of the process as a means of quantitatively estimating bromine under the circumstances indicated.

Researches upon Arseniuretted and Antimoniuretted Hydrogen, and their Relations to Toxicology. *By* Raphael Napoli, Royal Professor of Chemistry at Naples.

After Lassaigne had observed that nitrate of silver decomposes arseniuretted hydrogen with the formation of arsenious acid and the separation of metallic silver, Jacquelain proposed the chloride of gold for the same object, and Berzelius, in his 'Traité de Chimie,' says of this gas, "It precipitates the precious metals, as gold and silver, from their solutions, and is itself dissolved by the oxidation of its elements." Such a decomposition really takes place with arseniuretted hydrogen and the terchloride of gold, and also with the ferric and platinic chlorides; still no chemist, so far as I know, has explained the reaction.

The explanation which I now propose was suggested to me by

M. Nicolo Prestandrea of Messina, who wrote to me as follows:—"When arseniuretted hydrogen is passed through a solution of chloride of gold, we see that the gold is really reduced, and the arsenic dissolved as arsenious or arsenic acid. But as these bodies contain no oxygen, whence comes this element to oxidize the arsenic, unless from the decomposition of the water of the solution, whose hydrogen at the same time forms hydrochloric acid with the chlorine of the gold salt? This acid might be formed from the union of this chlorine with the hydrogen of the gaseous arseniuret, without any decomposition of water, in which case both gold and arsenic should be separated in the metallic state, according to the following equation:—

$$AuCl^3 + AsH^3 = 3HCl + Au + As.$$

So that the theory of this reaction is not yet made clear. In order to explain the facts just mentioned, we must suppose that arsenic, in its nascent state at least, can be dissolved by hydrochloric acid; such being the case, it would be easy to understand the formation of the acids of arsenic, the precipitation of the gold, and the production of hydrochloric acid. The gold having been reduced, according to the formula just given, there remains 3HCl and As, which would yield $AsCl^3$ and 3 equivs. of free hydrogen. The chloride of arsenic, when diluted with a large quantity of water, is decomposed into arsenious and hydrochloric acids."

On consulting Berzelius and other works of authority, I found it stated, on the one hand, that arseniuretted hydrogen is not altered by hydrochloric acid, and, on the other, that arsenic is not affected by hydrochloric acid. These statements seemed to render the proposed explanation inadmissible, but I have found by experiment that they are incorrect, and have arrived at the following conclusions,—first, arseniuretted hydrogen is almost totally decomposed by pure concentrated hydrochloric acid; and secondly, arsenic itself is soluble in this acid.

I passed the arseniuretted hydrogen gas generated in Marsh's apparatus through concentrated hydrochloric acid in a Liebig's bulb-tube; and after continuing the process for an hour, chloride of arsenic was found dissolved in the acid, thus proving the decomposition of the arseniuretted hydrogen*. To prove the second point, I took some crystallized metallic arsenic, washed it repeatedly with cold and pure hydrochloric acid, and when its surface was perfectly free from oxide, attacked it with boiling hydrochloric acid in a small retort, placing a little water in the receiver. On collecting the portion which distilled over, I found it to contain chloride of arsenic, and the liquid residuum in the retort contained a notable portion of the same chloride, thus showing the solubility of arsenic in hydrochloric acid.

These facts being well established by a series of repeated experi-

* The decomposition of arseniuretted hydrogen with hydrochloric acid is represented by $AsH^3 + 3HCl = AsCl^3 + 3H^2$, and is analogous to that of hydride of copper with the same acid; in each case a metallic chloride is formed, and the hydrogen of both compounds is set free. See Brodie's remarks on the latter reaction, in the 'Chemical Gazette' for 1853, p. 300.

ments, gave me an explanation of the reactions of arseniuretted hydrogen on the perchlorides of gold and iron, and the bichloride of platinum. The formulæ are as follows:—

$$AuCl^3 + AsH^3 = Au + AsCl^3 + H^3.$$
$$3Fe^2Cl^3 + AsH^3 = 6FeCl + AsCl^3 + H^3.$$
$$3PtCl^2 + 2AsH^3 = Pt^3 + 2AsCl^3 + H^6.$$

While studying the above reactions, I had occasion to repeat some observations which were made long since by Stromeyer, and appear to have been forgotten by chemists, but which serve to render more accurate the examinations for arsenic and antimony by Marsh's apparatus. The facts are these: arseniuretted and antimoniuretted hydrogen are both decomposed by pure and highly concentrated nitric acid, the former yielding water, nitrous vapour and soluble arsenic acid, while the latter gives insoluble antimonic acid, causing a turbidness in the liquid, which is increased by concentration. If then we pass a mixture of these two gases into nitric acid, and afterwards boil the turbid solution, a yellowish-white precipitate of antimonic acid separates; and by adding water and continuing the ebullition, the antimony is entirely thrown down, while the arsenic acid remains dissolved.

The two gases are also decomposed by aqua regia, with the formation of chloride of arsenic and perchloride of antimony. By a careful distillation of the mixture, the arsenical chloride passes over first, while the chloride of antimony remains in the retort, as has been shown by Malaguti and Sarzan. An analogous reaction is produced with strong hydrochloric acid, but with this difference, that the arseniuretted hydrogen is almost entirely decomposed, while the antimonial gas undergoes a less complete decomposition.

The applicability of these reactions to the concentration and separation of the arsenic and antimony, in the gas obtained by Marsh's apparatus, will now be apparent. Instead of burning or decomposing by heat the evolved gas, it is passed through a U-tube to dry it, and then, by means of a caoutchouc connector, into a Liebig's bulb apparatus, containing concentrated fuming nitric acid, which is to be heated by immersion in a bath of water or oil. Having assured ourselves of the purity of the gas evolved by the zinc and sulphuric acid, we add the suspected matter, and then pass the gas into the hot nitric acid, which completely decomposes in the manner just described any compounds of arsenic or antimony which may be evolved. If the nitric acid remains clear, we are almost sure of the absence of antimony. When the operation is finished, the contents of the bulbs are to be transferred to a small flask, the apparatus washed out with a little nitric acid, and the whole carefully evaporated to one-half. If there is no precipitate, the absence of antimony is certain; we then evaporate still further to remove the excess of acid, dilute the residue with water, and examine it like a pure solution of arsenic acid. Should the nitric acid appear turbid either before or after evaporation, antimony is present, and perhaps arsenic; in this case, after evaporating as before to a small bulk,

we add water and filter; the antimony remains behind in an insoluble condition, while the arsenic, if any were present, is held in solution, and both can be examined by the ordinary tests.

In the case of a mixture of arsenic and antimony, we may proceed in a different manner for their separation. Having prepared a small tubulated retort, to which can be adapted a small receiver, we introduce through the tubulure a tube reaching nearly to the bottom of the retort, in which is placed a small quantity of aqua regia composed of 2 parts of hydrochloric and 1 of nitric acid. The retort being gently heated, the gases from Marsh's apparatus are passed in a slow current into the aqua regia. In the reaction which takes place, any arseniuretted or antimoniuretted hydrogen will be decomposed, and chloride of arsenic or antimony formed. This operation finished, the tube is removed, the tubulure closed, and the receiver, partly filled with water, being attached, the acid liquid in the retort is gently distilled to one-half its volume. We then examine the water of the recipient, and if any arsenic is present, it will be found in the distilled liquid; if this metal be absent, we find nothing in the water, or at most some traces of antimony, in case the operation has not been well conducted. If the gas contained any antimony, it will all be found in the retort, in the state of perchloride.

I have not deemed it necessary to present the numerical results, which in repeated experiments have shown the great accuracy of these methods; but believing that chemists will at once recognise the value of the proposed processes, it is sufficient for me to have called their attention to the following facts, in part already known, and in part new.

1. The power of hydrochloric acid to dissolve and decompose arseniuretted hydrogen.

2. The solubility of metallic arsenic in the same acid when concentrated.

3. The explanation of the reactions of arseniuretted hydrogen with the perchlorides of gold and iron, and with the bichloride of platinum.

4. The decomposition of arseniuretted and antimoniuretted hydrogen by nitric acid and by aqua regia.

5. The application of these reactions to toxicological analysis, for the detection and separation of arsenic and antimony.—Silliman's *Journal*, September 1854.

On the direct Volumetric Determination of Ferridcyanogen in its Compounds. *By* E. Lenfsen.

The process is founded upon the following facts:—

Ferridcyanide of potassium and iodide of potassium have no action upon each other. But if strong muriatic acid be added to a moderately concentrated solution of the two salts (the decomposition only takes place imperfectly in dilute solutions), hydroferrocyanic acid and free iodine are produced, the latter remaining dissolved in the free hydriodic acid. The decomposition takes place in

accordance with the equation $Cfdy, 3H + IH = 2(Cfy, 2H) + I$. 1 equiv. of iodine, =126·88, consequently indicates 1 equiv. of ferridcyanide of potassium =329·33.

The application of the method is very simple. A solution of the ferridcyanide to be examined, such as the red prussiate of commerce, is prepared, containing from 2 to 4 grms. of the dry salt in 100 cub. centims.; 10 cub. centims. of this are then mixed with 10 cub. centims. or more of Bunsen's solution of iodide of potassium (1 to 10), and to the mixture pure concentrated muriatic acid, free from sulphurous acid and chlorine, is added until the fluid no longer acquires a darker colour on further additions. It is then immediately diluted with water, diluted sulphurous acid is added to it, and the determination of the free iodine is effected according to Bunsen's method.

If the solution does not become colourless on the addition of sulphurous acid, but remains rather yellowish, it is a sign that unreduced ferridcyanide of potassium has been present; the experiment must therefore be repeated, with the addition of more muriatic acid or iodide of potassium according to circumstances.

The following experiments show the very satisfactory degree of exactitude attained by this process:—

1. 0·3220 grm. of pure ferridcyanide of potassium set free 0·12323 grm. of iodine, representing 0·31985 of ferridcyanide of potassium =99·3 per cent.

2. 0·1578 grm. set free 0·06187 of iodine, representing 0·16590 of ferridcyanide of potassium =101·7 per cent.

3. 0·1805 grm. set free 0·0699 of iodine, representing 0·1814 of ferridcyanide of potassium =100·5 per cent.—Liebig's *Annalen*, xci. p. 240.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Liverpool, September 20th, 1854.

On a New Method of Alkalimetry. *By* Astley Paston Price, Ph.D., F.C.S., Chemical Assistant in the Laboratory of the Government School of Mines.

Having had occasion, some time since, to test the comparative value of the ordinary alkalimetrical processes, I was somewhat surprised at the discrepancies in the results I obtained, and also at the somewhat difficult and tedious manipulation necessary when comparatively accurate determinations were required. The most serious impediment in carrying out the usual alkalimetrical processes, arises, as is well known, from the liberation of carbonic acid, the presence of which, even in exceedingly small quantity, being sufficient to mask the point of saturation, and to prevent the indication of the presence of either an excess of acid or of alkali.

After having experienced the difficulties attendant on its presence,

and the almost impossibility of rapidly and entirely expelling the liberated carbonic acid from solution, it appeared to me most desirable to seek an alkalimetrical process, in which the carbonic acid should be expelled previous to determining the saturating power of the alkali under examination. It further appeared to me, that in the alkalimetrical processes now in use, there existed another very serious inconvenience, in that the per-centage of alkali was determined directly, and not indirectly; that is, that the alkali was estimated, and not the impurities which might be therein contained. This may perhaps be better understood by an example. Pure carbonate of soda contains about 58·5 per cent. of alkali, but commercial carbonate contains only about 50 per cent. Now in the several alkalimetrical processes employed in the arts, the 50 per cent. of alkali is estimated, and not the 8·5 per cent. of impurities, constituting, as these impurities invariably do, by far the smaller proportion of the commercial alkalies or alkaline carbonates.

In practice, it will, I believe, be found advantageous to employ a method which, by indicating the amount of impurities present, will give the available proportion of alkali.

As I have previously remarked, the primary difficulty to be overcome is the entire expulsion of carbonic acid, the presence of but a small quantity of which entirely prevents accurate determination, not only owing to the change of tint produced by its presence on a solution of litmus, but owing to the diminished sensibility of litmus thus tinted.

In the hope of avoiding those sources of error to which I have alluded, and of facilitating the determination of the true per-centage of alkali, I adopted a method of alkalimetry which in substance is the following:—To the alkali under examination is added a known excess of a normal solution of oxalic acid; and after the expulsion of carbonic acid from the solution by boiling, the excess of oxalic acid remaining is determined by means of a standard solution of ammonia.

Some objection might be made to the employment of a solution of ammonia; but it will be found that a dilute solution of ammonia, if kept in properly constructed apparatus, will remain more constant than might be expected. The standard solutions of ammonia and of oxalic acid are most easily prepared by means of a standard solution of sulphuric acid, care being taken that perfectly pure acid be employed, and that the amount of real acid be carefully determined.

Having prepared the standard solutions of a desired strength, the determination of an alkali or of an alkaline carbonate may be thus effected:—10 grs. of an alkaline carbonate, carbonate of soda for example, after having been placed in a flask, a solution of oxalic acid corresponding to 10 grs. of pure carbonate of soda is added; the solution is then boiled until the expulsion of carbonic acid be effected, when the solution is diluted with distilled water; and after the addition of a few drops of a solution of litmus, the excess of oxalic acid is determined by a standard solution of ammonia. The excess of oxalic acid remaining will of course indicate the impurities

present, or the absence of alkali, which, by deduction from the quantity originally taken, will give the amount of available alkali.

Care must be taken that the solution be only tinted with litmus, and not too deeply coloured, as the more feeble the coloration within certain limits, the more easily detected is the change of tint produced by an excess of alkali or acid.

I have found it necessary to employ distilled water, failing, as I have done, to obtain accurate results with other water, owing to the presence of carbonic acid. The preparation of standard solutions is so well understood, that it is unnecessary to enter into further details.

The apparatus I have found most convenient for containing and preserving standard solutions, and more particularly solutions of ammonia, consists of a vessel similar to a wash-bottle, to which is attached an India rubber bulb; so that when it is desired to fill the burette, it is only necessary to compress the bulb. This arrangement affords great facility for replenishing the burette; and by placing a piece of India rubber tubing, closed at one end, on the jet, an air-tight reservoir for the solution is obtained.—*Communicated by the Author.*

On the Action of Gallic and Tannic Acids on Iron and Alumina Mordants. *By* Prof. CALVERT.

The author drew the following conclusions from the facts contained in his communication:—1st, that there can be no doubt that tannic acid is the matter in tanning substances which produces black with iron mordants; 2nd, that the reason of gallic acid producing no black dye is, that it reduces the peroxide of iron in the mordant, forming a colourless and soluble gallate of protoxide of iron; 3rd, that gallic acid has the property of dissolving hydrate of alumina, and also of separating alumina mordants from the cloth on which they are fixed; 4th, that the reason of extracts of tanning matter losing their dyeing properties is, that the tannin is transformed into gallic acid; 5th, that gallic acid possesses the property of dissolving iron, and thus lays claim to the character of a true acid, whilst tannin, not having this action, appears to be in reality a neutral substance.—*Athenæum.*

On the Action of Citric, Tartaric, and Oxalic Acids on Cotton and Flax Fibres under the Influence of Dry Heat and Pressure of Steam. *By* Prof. CALVERT.

The author observed, that when 2 to 4 parts of these acids are dissolved in 100 parts of water, and linen or cotton dipped into the solution obtained, and afterwards dried in the air, they, on exposure to certain temperatures, completely destroy the tenacity of the fibre. This action of organic acids is interesting when it is known that it takes place even at the low temperature of 180°, 212°, and 260° F. He also found that cotton and flax fibres, when prepared as above and then submitted to the influence of steam of 3 lbs. pressure, were destroyed.—*Athenæum.*

THE CHEMICAL GAZETTE.

No. CCXCI.—December 1, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Platinum Bases. By C. CLAUS.

PROF. CLAUS of Dorpat has examined some new bases. He endeavoured particularly to prepare bases in which, instead of metallic oxides of the formula RO, those of the formula $R^2 O^3$ are contained. By the comparison of the properties of these bodies, the author has arrived at a new mode of viewing these compounds, which is certainly interesting. Thus he comes to the conclusion, that the basicity of these bodies is not derived from the ammonia but from the metallic oxides.

The author first examines the well-known green salt of Magnus, $PtCl, NH^3$, which is regarded by most chemists as consisting of ammonia and protochloride of platinum. He then turns to that mode of viewing it derived from the ammonium theory, according to which it is a chloride of ammonium, in which 1 equiv. of hydrogen is replaced by $Pt, -NH^3 Pt + Cl$.

If the chlorine in the latter formula be replaced by oxygen, we obtain Reiset's second base, $NH^3 Pt, O$, which, to suit the ammonium theory, may be regarded as oxide of ammonium in which 1 equiv. of hydrogen has been displaced by platinum.

The author however considers the circumstance, that this base may combine with a second equivalent of ammonia without changing its capacity of saturation, thus forming the so-called first platinum base of Reiset, as an important reason against the application of the ammonium theory to these bases; he expresses himself very strongly in opposition to Gerhardt's mode of treating this subject, and establishes the following law as the foundation of his own method of bringing the composition of these bodies into regular formulæ:—

Ammonia may play a passive part in regard to its basicity in many compounds, and act, like water, as basic and non-basic ammonia.

According to this view, the platinum bases may be regarded as compounds of passive ammonia with metallic oxides, in which the capacity of saturation depends upon the latter. In this way the formulæ of the platinum bases may be educed according to a single fundamental type, and all the contradictions which attended the view hitherto entertained may be got rid of. At the same time the formulæ are greatly simplified, as may be seen from the following table:—

Reiset's second base, as the type	PtO, NH^3.
Oxyacid salts of this base (X indicates the acid)	PtO, NH^3+X.
Chloride	Pt, NH^3+Cl or $PtCl+NH^3$.
Reiset's first base	$PtO, 2NH^3$.
Oxyacid salts	$PtO, 2NH^3+X$.
Chloride	$Pt, 2NH^3+Cl$ or $PtCl+2NH^3$.
Gerhardt's base	PtO^2, NH^3.
Oxyacid salts :—*a*, basic	PtO^2, NH^3+X.
b, neutral	PtO^2, NH^3+2X.

Compounds occurring in Gros' *Salts.*

Base	$PtO^2, 2NH^3$.
Oxyacid salts	$PtO^2, 2NH^3+2X$.
Chloride	$Pt, 2NH^3+2Cl$ or $PtCl^2+2NH^3$.
Gros' salts are double salts of the above oxyacid salts with the chloride	$PtO^2, 2NH^3+2X$. / $Pt, 2NH^3+2Cl$.
Gros' chloride	$Pt, 2NH^3+2Cl$ / $Pt, 2NH^3+2Cl = PtCl^2, 2NH^3$.
Skoblikoff's base *a*	IrO, NH^3.
Sulphate	IrO, NH^3+SO^3.
Chloride	Ir, NH^3+Cl or $IrCl, NH^3$.
Skoblikoff's base *b*	$IrO, 2NH^3$.
Oxyacid salts	$IrO, 2NH^3+X$.
Chloride	$Ir, 2NH^3+Cl$ or $IrCl, 2NH^3$.
Double salts	$IrO^2, 2NH^3+2X$. / $Ir, 2NH^3+2Cl$ or $IrCl^2+2NH^3$.
Hugo Müller's base *a*	PdO, NH^3.
Oxyacid salts	PdO, NH^3+X.
Chloride	Pd, NH^3+Cl or $PdCl+NH^3$.
Hugo Müller's base *b*	$PdO, 2NH^3$.
Oxyacid salts	$PdO, 2NH^3+2X$.
Chloride	$Pd, 2NH^3+Cl$ or $PdCl+2NH^3$.

Rajewski's salts would fall very readily into these formulæ, if we might make some corrections in the results of the analyses. These salts have evidently a composition analogous to those of Gros; they are double salts, in which however the quantity of the oxyacid salt exceeds that of the chloride. Several of Gerhardt's salts appear to be compounds of salts of the mono-ammoniacal and biammoniacal platinum bases.

The formulæ published by the author are certainly not new in their form, for Gmelin has already employed them in his 'Handbuch;' but their sense, as explained by the author, is evidently different.

The consideration of the constitution of the platinum bases according to the above principles and formulæ also accounts for the formation of Gros' salts, whilst the previous theory left this in complete obscurity. How is the production of an amidogen compound by the action of nitric acid upon Magnus' salt to be explained? If the new formula be accepted, there is no difficulty in its explanation. Nitric acid converts the protochloride of the salt partly into perchloride, and partly into an oxyacid salt, which contains oxide of platinum, exactly as it would act upon the simple protochloride. For this reason alone the formulæ above given have more probability than the previous ones; but we have yet another reason for being sure that peroxide and perchloride of platinum occur in these salts,

for when sulphuretted hydrogen acts upon them, sulphur is separated, indicating the reduction of an oxide into a lower one. We also get an explanation of the fact observed by Reiset, that the chloride of his base, $PtCl, 2NH^3$, is converted by the action of chlorine into the chloride of Gros' base, $PtCl^2, 2NH^3$, that is to say, from the protochloride into the perchloride. Lastly, the well-known fact that Reiset's first base, $PtO, 2NH^3$, is decomposed by heat into his second base, PtO, NH^3, and ammonia, NH^3, also receives a satisfactory explanation.

The combinations of ammonia with some oxyacid salts also support the view put forward as to the passive state of ammonia; this is particularly remarkable in the compounds recently prepared by Fremy, of 1 equiv. of the oxides of cobalt with 2 to 6 equivs. of ammonia, the amount of acid in which is always dependent on the amount of oxygen in the metallic oxide, and never on the number of equivalents of ammonia. Amongst these there are some, especially those of the formulæ $Co^2O^3, 5NH^3 + 3NO^5$ and $Co^2O^3, 5NH^3 + 3SO^3$, which are constituted exactly like the analogous salts of the rhodium and iridium bases prepared by the author; also $Co^2O^3, 6NH^3 + 3NO^5$; $Co^2O^3, 6NH^3 + 3SO^3$, and the chloride, $Co^2, 6NH^3 + 3Cl$. In all these salts the equivalents of acid are dependent on the equivalents of oxygen in the oxide of cobalt. It does not appear from Fremy's statements whether these salts were neutral; the author's salts, on the contrary, were perfectly neutral, and their ammoniacal bases allowed themselves to be transferred to other acids, which indubitably proves that in these cases the ammonia played a passive part in regard to its basicity. The sulphate of copper and ammonia, the formula of which, according to this view, must be written $CuO, 2NH^3 + SO^3$, also very probably belongs to this group of compounds, except that it has a basic reaction. This reaction depends upon the circumstance, that this salt is always in a state of decomposition, and constantly gives off small portions of free ammonia until it is completely decomposed.

The mercurial base, $NH^2Hg, 3HgO, 3HO$, prepared by Millon, which appears at the first glance to contradict the author's views, is found on closer investigation to afford it support. Here we have only to consider that this is an amide, which must be regarded as an ammonia in which 1 equiv. H is replaced by Hg; there is no doubt that it acts a passive part in this case, as the 3 equivs. of oxide of mercury form the usual basic salts, formerly called turpeths, with 1 equiv. of an oxyacid. Millon's salts are consequently nothing but turpeths combined with mercurial amide.

The author however finds the principal support for his views in the composition of the following new bases and their salts, which he has prepared. The formulæ of these bodies are as follows:—

Rhodium base	$Rh^2O^3, 5NH^3$.
Chloride	$Rh^2, 5NH^3 + Cl^3$ or $Rh^2Cl^3 + 5NH^3$.
Carbonate	$Rh^2O^3, 5NH^3 + 3CO^2$.
Sulphate	$Rh^2O^3, 5NH^3 + 3SO^3$.
Nitrate	$Rh^2O^3, 5NH^3 + 3NO^5$.

Iridium base	$Ir^2O^3, 5NH^3$.
Chloride	$Ir^2, 5NH^3+3Cl$ or $Ir^2Cl^3+5NH^3$.
Carbonate	$Ir^2O^3, 5NH^3+3CO^2$.
Sulphate	$Ir^2O^3, 5NH^3+3SO^3$.
Nitrate	$Ir^2O^3, 5NH^3+3NO^5$.

These cannot be represented in any way according to the ammonium theory; they prove in the most distinct manner the two principal laws of the author,—the passivity of ammonia, and the dependence of the capacity of saturation of the bases upon the metallic oxides. The number of equivalents of ammonia which enter into these compounds is by no means accidental; it depends upon the number of equivalents of water which occur in the hydrates of the metallic oxides or metallic salts, which form the constituents of these compounds; thus from the hydrate of sesquioxide of rhodium, Rh^2O^3+5HO, the base $Rh^2O^3+5NH^3$ is formed; and from the protonitrate of cobalt, CoO, NO^5+5HO, the salt $CoO, NO^3+3NH^3, 2HO$. The number of examples cannot at present be greatly increased, as the composition of the constituents, as regards their amount of water, is not yet exactly known, but many more will be brought out hereafter.—*Bull. de St. Pétersb. Cl. Phys. Math.*, xiii. p. 97.

On the Tungstates. *By* Dr. W. Lotz.

Laurent has proposed the following formulæ for the tungstates:—

1. Tungstates .... WO^4R,	2. Isotungstates.... W^2O^7R,
3. Metatungstates $W^3O^{10}R$,	4. Paratungstates .. $W^4O^{14}R^2$,
5. Homotungstates $W^5O^{16}R$,	6. Polytungstates .. $W^6O^{21}R^3$.

The first type is composed of those known as neutral salts, the fourth of those usually regarded as bitungstates. Besides these two series, Marguerite has made known the tetra-, penta- and hexatungstates.

The author has recently investigated a series of salts, prepared from the ammoniacal salt, which he obtained in a state of purity, by decomposing the wolfram of Zinnwald with concentrated muriatic acid and a little nitric acid, decanting with water, dissolving the residue of impure tungstic acid (which is especially contaminated by iron) in ammonia, and crystallization. In recrystallization, an ammoniacal double salt containing iron has to be separated; for this purpose some free ammonia is added. In this manner

Tungstate of Ammonia, $(AmO)^3+7WO^3+6H$, is obtained. This is probably a double salt$=2(AmO+2WO^3)+(AmO+3WO^3)+6H$, to which, according to Svanberg and Struve, there is a corresponding salt in the series of molybdates, $2(AmO, 2MoO^3)+(AmO+3MoO^3)+3HO$. It is probably the same salt for which Laurent gave the formula $W^4O^{14}Am\frac{1}{3}^0H\frac{2}{3}+Aq$, or in entire equivalents$=(AmO)^5+(WO^3)^{12}+10HO$.

This salt is stable at ordinary temperatures. At 212° F. it loses a portion of its water of crystallization without falling to powder; when exposed to a red heat, yellow tungstic acid is left, still retaining the

form of the salt. It dissolves slowly and with difficulty in water. When put solid into water, heated and constantly stirred, it appears to be nearly insoluble. On the average, 1 part dissolves in 26·1 parts of water at 51°·2 F., in 5·8 parts at 212° F. When the watery solution is boiled, ammonia is evolved, and a new and much more soluble compound is produced. The analysis of the salt gave,—

WO^3	85·93	86·07	7	86·02
AmO	8·10	8·03	3	8·26
HO	5·97	5·90	6	5·72

Ammonia Salt, $2(AmO + 2WO^3) + (AmO + 3WO^3) + 3HO$.—If the solution of tungstate of ammonia be evaporated at a rather strong heat, a salt crystallizes, which contains less water than the preceding. When dissolved in water and evaporated at a more gentle heat, it is again converted into the salt with 6 atoms of water. Berzelius considered it identical with the preceding salt; Laurent gave it the formula $W^4\,O^{14}\,Am^{\frac{1}{3}}\,H^{\frac{2}{3}} + Aq$. Its analysis gave—

WO^3	88·53	7 =	10155·25	88·56
AmO	8·33	3	974·94	8·50
HO	3·14	3	337·44	2·90

If it be attempted to form tungstate of ammonia by mixing a hot solution of muriate of ammonia with a simple alkaline tungstate, the salt which is obtained always contains some of the fixed base. The experiment was made with tungstate of soda.

The following salts are obtained by the double decomposition of the ammoniacal salt first described with other salts. They all, when freshly precipitated, dissolve in a very small quantity of water on the addition of a drop of nitric acid, as was previously observed by Laurent. The fluid generally sets, after standing for some time, into a stiff yellowish-white magma. Muriatic acid has a similar action. The salts of lead, silver, and mercury do not dissolve in water containing nitric acid. These salts all contain water. After calcination, they are generally of a sulphur-yellow colour, but become dark yellow on being heated.

Tungstate of Baryta, $(BaO)^3 + 7WO^3 + 8HO$, is a white pulverulent precipitate, which fuses at a strong red heat into a hard bladdery mass. At 212° F. it loses 4 equivs. of water, and another 4 equivs. at a red heat. Analysis of the calcined salt:—

WO^3	..	..	7 =	10155·25	77·99
BaO	21·33	21·02	3	2865·87	22·01

Tungstate of Strontia, $(SrO)^3 + (WO^3)^7$, is a white pulverulent precipitate. It still contains some ammonia after washing, and loses 4·76 per cent. of water at 212° F. This, after the deduction of the quantity of ammonia indicated by analysis, amounts to 4 or 5 atoms. Analysis of the dried salt:—

WO^3	82·72	..	7 =	10155·25	83·98
SrO.....	14·62	2·26	3	1937·79	16·02
AmO	0·66	2·20			

Tungstate of Ammonia and Magnesia, $2(MgO, 2WO^3) + AmO\ 3WO^3 + 10HO$.—A solution of sulphate of magnesia does not produce a precipitate with tungstate of ammonia. If the concentrated solutions be mixed whilst hot, small, white, nacreous crystals, difficult of solution in water, are obtained. Analysis:—

WO^3	83·65	7 =	10155·25	83·78
MgO	4·33	2	516·28	4·26
AmO	2·46	1	324·98	2·68
HO.....	9·41	10	1124·80	9·28

Tungstate of Ammonia and Zinc, $2ZnO + AmO + 7(WO^3)$, forms small snow-white needles. Analysis:—

WO^3	78·36	7 =	10155·25	78·38	86·20
ZnO	7·80	2	1013·18	7·82	
AmO.....	2·56	1	324·98	2·51	
HO	11·28	13	1462·24	11·29	

At 212° F. the salt loses 8 atoms HO, which from calculation amount to 6·94 per cent. Experiment gave 6·88 per cent.

Tungstate of Ammonia and Cadmium, $(AmO)^3 + 7WO^3 + 4(3CdO + 7WO^3) + 35HO$, is a voluminous white precipitate, which becomes gray and afterwards orange-yellow when heated, remaining light yellow when cooled. Analysis:—

WO^3	78·05	7 =	10155·25	77·82	
CdO	14·62	$\frac{1}{5}$	1912·24	14·65	
AmO.....	1·54	$\frac{3}{5}$	194·99	1·49	7·52
HO	.. 7·33	7	787·36	6·03	

Prototungstate of Manganese, $3MnO + 7WO^3$, is a white slimy precipitate, with a yellowish tinge; it becomes straw-yellow when heated to redness. Analysis:—

WO^3	..	7 =	10155·25	88·39
MnO	11·42	3	1334·05	11·61

Prototungstate of Nickel has the formula $2(NiO^2\ WO^3) + NiO, 3WO^3$.

Tungstate of Lead, $2(PbO + 2WO^3) + PbO, 3WO^3$, is a white flocculent precipitate, which afterwards becomes pulverulent; it is insoluble in water, even on the addition of a very little nitric acid; insoluble also in tungstate of ammonia and in nitrate of lead; it dissolves in caustic soda and in boiling phosphoric acid. Analysis:—

WO^3.....	..	..	7 =	10155·25	70·82
PbO	30·21	29·66	3	4183·93	29·18

Tungstate of Alumina forms a caseous precipitate, and dries to a glassy mass. The salt, dried at 212° F., had the constitution Al^2O^3, $7WO^3 + 9HO$. Neutral tungstate of alumina is a white flocculent precipitate, soluble in sulphate of alumina and potash, soda, ammonia, phosphoric acid, oxalic acid, and tartaric acid.

Tungstate of Chromium, $Cr^2O^3 + 7WO^3$, is thrown down as a pulverulent precipitate of a pale grayish-green colour, by the double

decomposition of tungstate of ammonia and sublimed perchloride of chromium. The neutral salt is a pale green precipitate.

Tungstate of Iron is obtained like the preceding salts, by means of perchloride of iron. It is a tawny precipitate.

Tungstate of Tin, $(SnO^2)^9+13WO^3$, is obtained by means of perchloride of tin, in the same manner as the preceding salts. The formula appears to indicate that hydrated oxide of tin is precipitated along with it.

The *Octahedric Tungstate of Ammonia*, $AmO+3WO^3+5HO$, of Marguerite, does not, according to the author, possess this composition; it is $2(AmO,4WO^3)+15HO$. This is the salt to which Laurent ascribes the formula $WO^3\,H^{10}\,Am\frac{5}{3}\,H\frac{1}{3}+5Aq$, and which he refers to the *type métatungstique*.

The salt, according to the author, forms acute quadratic octahedra with the following modifications:—P; P and 0P; P and 0P and $\infty P\infty$. Nacreous, with an indistinct laminar cleavage in the direction of the latter faces. The analysis of this salt gave—

WO^3.....	83·02	82·92	8 =	10606·00	83·24
AmO.....	4·73	4·63	2	649·96	4·66
HO	12·25	12·45	15	1687·20	12·10

This salt (indicated by B in the following remarks) loses almost the whole of its water of crystallization at 212° F. It is therefore considerably more soluble than the salt $A=(AmO)^3,7WO^3$, although containing more of the insoluble tungstic acid. From a comparison of the properties of the two salts, it appears to contain a different modification of tungstic acid than that of the latter salt. The salt A immediately gives a white precipitate with an excess of muriatic or nitric acid at ordinary temperatures; this becomes yellow by boiling, and before boiling dissolves again only in an exceedingly great excess of acid. The salt $AmO,4WO^3$ gives no turbidity with either acid in the cold or at a boiling heat. It is only by continued boiling that a precipitate of yellow pulverulent WO^3 is produced. But if, before the addition of the acid, a caustic alkali or an alkaline carbonate be added to the solution, a white precipitate is immediately produced by acids; this acquires a yellow colour by boiling. Neither caustic alkalies nor alkaline carbonates produce, as stated by Marguerite, any precipitate in the solution of the salt $AmO,4WO^3$.

The salt $AmO^3,7WO^3$ furnishes the brown precipitate already described with muriatic acid and ferrocyanide of potassium. The other salt, B, gives no precipitate; but a precipitate is immediately produced when the mixed acid fluid is rendered alkaline, and then again acidulated. The salt A gives a white flocculent precipitate with solutions of silver; this is insoluble in water, but dissolves in ammonia, and crystallizes from this solution. The other salt, contrary to Laurent's statement, gives no precipitate. The salt A furnishes precipitates with the salts of the alkaline earths and of metallic oxides; the salt B only with protosalts of lead and mercury. Ammouia converts the salt B into salt A, so that after being treated with this reagent, it behaves with salts and acids like the latter salt.—Liebig's *Annalen*, xci. p. 49.

On the Action of Iodide of Phosphorus upon Glycerine.
By MM. BERTHELOT *and* DE LUCA.

I. If 1 part of crystallized iodide of phosphorus and 1 part of syrupous glycerine be mixed together, a very brisk reaction soon takes place; a gas is evolved, two liquids distil over, and a portion of the matter remains in the retort.

The gas is propylene, $C^6 H^6$. The two liquids are water and iodized propylene, $C^6 H^5 I$. The substance remaining in the retort is formed of undecomposed glycerine, of iodine, of an iodized organic substance in small quantity, of oxyacids of phosphorus, and a trace of red phosphorus. These different bodies are produced in the following proportions:—

1. With 1 equiv. of iodide of phosphorus and variable weights of glycerine, 1 equiv. of iodized propylene and 4 equivs. of water are obtained.

2. To obtain 1 equiv. of propylene, from 9 to 18 equivs. of iodide of phosphorus must be employed. The production of propylene is consequently of secondary importance compared with that of the iodized propylene.

3. The substance remaining in the retort varies in its nature with the relative proportions of the iodide of phosphorus and glycerine. By employing 100 parts of iodide of phosphorus and 100 parts or more of glycerine, the products are as indicated above, the glycerine forming the greatest portion of the mass. But if only 64 parts or less of glycerine are employed with 100 parts of iodide of phosphorus, the residue in the retort consists of a solid, black, insoluble substance.

The point at which this change in the reaction takes place nearly corresponds with the following proportions,—2 equivs. of glycerine to 1 equiv. of iodide of phosphorus.

4. One-half of the iodine has nothing to do with the formation of the iodized glycerine; this iodine exists in the retort in various forms, but it may be considered that it is almost all in a free state.

According to these different determinations, it appears that the principal reaction exerted by iodide of phosphorus upon glycerine must be represented by the following equation:—

$$PI^2 + 2C^6 H^8 O^6 = C^6 H^5 I + 4HO + I + (C^6 H^8 O^6 + PO^3 - HO)^*.$$

The production of the iodized propylene is owing to a reducing action exerted by the iodide of phosphorus upon the oxygen of the glycerine.

II. We have particularly studied the two essential products of this reaction,—iodized propylene and propylene.

Iodized Propylene, $C^6 H^5 I$, forms almost the whole of the volatile compound. To obtain it pure, this compound is distilled, and the portion passing at 214° F. collected separately. It is a liquid insoluble in water, soluble in alcohol and æther, possessing an ætherial

* The parenthesis represents the oxygenated acids of phosphorus, mixed and combined with the excess of glycerine. This glycerine may be isolated by treating the mixture with oxide of lead.

and somewhat alliaceous odour. It rapidly acquires colour by the action of air and light, and then diffuses exceedingly irritating vapours. Its density at 60°·8 F. is 1·789.

This body presents various interesting reactions, which we are still investigating. The following are some of them:—

Aqueous ammonia, by acting upon iodized propylene for forty hours at 212° F., entirely decomposes it. If the products of this reaction be distilled with potash, a very volatile alkali, soluble in water, is obtained; it possesses a fishy ammoniacal odour; it forms a deliquescent muriate, which is soluble in absolute alcohol, and also a crystalline platinum double salt, which is soluble in boiling water.

The constitution of this alkali is represented by the formula $C^6 H^9 N$. From its analysis, its properties and its origin, it appears to be *propylamine*.

Fuming nitric acid instantly destroys iodized propylene, precipitating the iodine.

Sulphuric acid, which has no action in the cold, carbonizes it when heated, disengaging a small quantity of propylene. If some iodized propylene be put into a bottle containing a little zinc and dilute sulphuric acid, and the whole be slightly heated, the iodized propylene is decomposed, and the gas evolved contains one-fourth of propylene,—

$$C^6 H^5 I + 2Zn + HO = C^6 H^6 + ZnI + ZnO.$$

This process enables us to obtain propylene from the iodized propylene, that is to say, to substitute hydrogen for the iodine.

This inverse-substitution may be effected in a more complete and advantageous manner, by the intervention of the peculiar affinities of mercury for iodine. Thus if we put some mercury into a test-tube, and pour upon it a little iodized propylene, water and sulphuric, or, which is better, concentrated muriatic acid, the mercury is attacked, and a gas soon begins to be evolved. The reaction continues until the complete decomposition of the iodized propylene. In this manner nine-tenths of the iodized propylene may be converted into propylene. The reaction is as follows:—

$$C^6 H^5 I + HCl + 4Hg = C^6 H^6 + Hg^2 Cl + Hg^2 I.$$

It allows us to obtain propylene in abundance.

Propylene, $C^6 H^6$, may be obtained in a state of purity, either by collecting the gas disengaged during the reaction of glycerine upon iodide of phosphorus, or by the action of mercury and muriatic acid upon iodized propylene. As this gas appears to us, in consequence of the facility with which it is produced, to be fitted for study in lectures and laboratories, we shall briefly indicate the mode of preparation.

The iodide of phosphorus is prepared by Corenwinder's method, by dissolving 25 grms. of phosphorus and 200 grms. of iodine in sulphuret of carbon, and evaporating the solvent in a stream of dry carbonic acid. 50 grms. of iodide of phosphorus, PI^3, and 50 grms. of syrupous glycerine (commercial glycerine, purified and evaporated

to 160°) are mixed in a tubulated retort. The reaction is commenced by the assistance of a gentle heat. About 30 grms. of iodized propylene condense in the cooled receiver.

This crude product, put into a small flask with 150 grms. of mercury and from 50 to 60 grms. of fuming muriatic acid, soon evolves propylene, especially when assisted at the commencement by a very gentle heat. By this means about 3 litres of gaseous propylene are obtained:—

	Calculated from formula $C^6 H^6$.
10·0 vols. of propylene analysed by detonation furnished	10·0 vols.
30·4 vols. of carbonic acid, by the absorption of.....	30·0 vols.
45·2 vols. of oxygen.....	45·0 vols.

This gas is absorbed by fuming or concentrated sulphuric acid. Crystallizable acetic acid dissolves 5 vols. of it. An acid solution of protochloride of copper dissolves $1\frac{1}{2}$ vol. Bromine absorbs and combines with it. If a little iodine be put into a flask filled with propylene, and the mixture exposed to the sun for an hour, a very heavy liquid is rapidly formed, which may be purified by shaking with a little potash.

This liquid is *iodide of propylene*, $C^6 H^6 I^2$. When recently prepared, it is colourless, and possesses an ætherial odour; but the action of the air, and especially of light, colour it rapidly, and it then exerts a very irritating action upon the eyes. Its density at 65°·3 F. is 2·490. When cooled to 14° F., it remains liquid. It is decomposed by heat.

Heated with potash and alcohol, it is decomposed, reproducing propylene in abundance.—*Comptes Rendus*, Oct. 16, 1854, p. 745.

New Researches on Starch. *By* M. A. Béchamp.

During some researches upon xyloidine, the author has studied the action of nitric acid, sulphuric acid, crystallizable acetic acid, chloride of zinc, and caustic alkalies upon starch. He considers that the insolubility of starch is not dependent upon its organization, and that the substance soluble in cold water, known to chemists as *dextrine colourable by iodine*, is a modification of starch intermediate between it and pure dextrine.

If starch be treated with very concentrated nitric acid (a mixture of equal parts of $NO^5 4HO$ and $NO^5 HO$), it is first of all converted into a thick paste, which at last dissolves in an excess of acid*. The addition of a sufficient quantity of concentrated alcohol separates the whole of the starch in the form of a sticky mass, which, when washed with alcohol, is reduced to a white powder, perfectly neutral to litmus-paper. This substance is slightly soluble in cold water, but nine-tenths of it are insoluble in that fluid. But if the sticky mixture of starch and acid be left to itself for from forty-eight to sixty hours, or heated until the appearance of reddish vapours, it

* The liquid obtained is entirely soluble in cold water, so that no xyloidine can have been formed.

becomes completely liquefied, and the starch may still be entirely separated by concentrated alcohol. The product, washed with alcohol to remove adherent acid, is then completely soluble in cold water. In all cases both the soluble and insoluble matters acquire a blue colour by iodine.

A thick mixture of starch and concentrated sulphuric acid, $SO^3 HO$, treated with alcohol after about four minutes' contact, behaves exactly like the mixture of starch and nitric acid; the starch is entirely separated, and becomes partially soluble in cold water. But when the mixture is left for half an hour, the starch separated by the alcohol has become completely soluble in cold water.

Crystallizable acetic acid, heated to 212° F. with starch, in a sealed tube, converts it into the soluble modification in from three to five hours; the starch grains are not deformed or dissolved; they are merely split (but not exfoliated) in the region opposite to the tube. Ordinary acetic acid acts more quickly upon starch, and may convert it into dextrine under the same circumstances.

A concentrated solution of fused chloride of zinc, free from acid, converted starch into a paste in the cold. This paste liquefies in a few hours when heated to 212° F. The mixture may be heated to 284° F. without the formation of any trace of dextrine; but the starch separated from this zinc solution by alcohol may, according to the duration of the reaction, become entirely soluble in cold water.

Starch heated in *a very concentrated* solution of caustic potash or soda, loses the whole of its [?] nitrogen in the form of ammonia. The author confirmed this evolution of ammonia, not only by test-paper, but also by converting this alkali into the double chloride of platinum and ammonium. When the caustic alkali is saturated with acetic acid, the addition of alcohol separates the whole of the starch. A small quantity has become soluble, but the greater part remains insoluble, not only in cold, but even in boiling water. Dextrine is never formed by the action of caustic alkalies. The insoluble disorganized starch no longer forms a paste with hot water, but by the action of acids it may be converted into soluble starch, and afterwards into dextrine. The author's memoir contains details showing the insensible passage of insoluble starch to the state of soluble starch.

He considers that his experiments leave no doubt that starch is insoluble in all its parts, although formed of strata of different ages, the most recent being the most readily altered.

The following properties of soluble starch serve to distinguish it from dextrine:—

1. It is coloured blue by tincture of iodine.

2. Tannic acid produces a precipitate with it, as in the apparent solution of ordinary starch.

3. It causes turbidity in lime-water, and produces an abundant precipitate in baryta-water. Carbonic acid separates it unchanged from its baryta componnd.

4. Its molecular rotatory power is much greater, but in the same direction; it is $[\alpha]j=210°$.

The solution of soluble starch passes pretty readily through the pores of an animal membrane.

If starch-paste be boiled in water and filtered, the filtrate will not contain more than 0·338 per cent. of starch. This solution becomes turbid when it is concentrated on the water-bath; the starch separates, and the liquid when filtered does not contain more dissolved matter than before the evaporation. A solution of soluble starch, on the contrary, may be evaporated to a syrupy consistence without turbidity.—*Comptes Rendus*, Oct. 2, 1854, p. 653.

On Dr. Price's *New Method of Alkalimetry.*

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Manchester, Nov. 17, 1854.

Sir,—In the 'Chemical Gazette' for November 15, occurs a memoir by Dr. Price on a new method of alkalimetry, depending on the decomposition of a carbonate by oxalic acid in excess. It appears to me that there is an objection to this plan, from the fact of oxalic acid also decomposing chloride of sodium, quadroxalate of soda being formed, and muriatic acid being expelled by the boiling. Thus, in case of a commercial soda ash, which always contains chloride of sodium, more oxalic acid will have been consumed than would decompose the carbonate, and the amount of soda would be estimated too high.

I am, Sir,
Yours respectfully,
James Higgin.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Substitutes for Tartaric Acid in Dyeing.
By Prof. Bolley.

In consequence of the present high price of tartaric acid, the author has examined the means by which this acid may be replaced. Ever since the discoveries of Daniel Köchlin, of Mühlhausen, brought the variety of patterns of the Scotch bandana handkerchiefs to such great perfection, tartaric acid has always been employed as the acid reagent by which to determine the action of the chlorine of the vat upon particular spots. Even supposing that the introduction of a substitute was not absolutely necessary, yet there is certainly no occasion to give up the hope of finding one.

In order to test the applicability of some new discharge-agents which have been recently proposed, it is necessary to inquire a little more closely what is required of them:—

1. The discharge-agent has to decompose the chloride of lime, that is, to set free the chlorine or hypochlorous acid. 2. To dissolve the mordants by means of which the colour is fixed. A number of acid bodies may be employed for both these purposes; and the

choice would indeed be very great, if it were not greatly narrowed by another series of considerations. These are,—

1st, the acid must be readily soluble; 2nd, it must be one which will not attack the fibres; 3rd, nor one which would act too powerfully upon the metal of the plates; 4th, as a portion of it remains in the chloride of lime vat, it must be of such a nature as not to injure the permanent activity of the chlorine vat.

Prof. Bolley particularly recommends phosphoric acid for this purpose. He was led to this by the process recently patented by Messrs. Kopp and Gatty of Manchester, in which arsenic acid is employed, and by which patterns are produced, which are not only equal to those made with tartaric acid, but even excel them in sharpness and whiteness. With such evident advantages, arsenic acid would soon displace tartaric acid, but for the insuperable evils attending its employment, in the extraordinary activity with which it attacks the skin, and destroys the nails of the operators, &c. Besides this caustic action upon the bodies of those employing it, its violently poisonous properties must also be taken into consideration.

Perchloride of tin has been repeatedly employed in the place of tartaric acid. That perchloride of tin, which contains much free acid, such as all the fluid chloride of commerce, both can and must discharge, follows as a matter of course; but it is equally clear that great caution is necessary in its employment. The author has already referred to a preparation, met with in commerce in a solid state, in which he found an average amount of 36 per cent. of tin. This, which although not quite free from acid, yet contains free acid only in small quantities, is now much used by our printers. According to information received from printing establishments which employ this salt, 11 parts of it replace 10 parts of tartaric acid; and as it costs about 135 francs the hundredweight, its price is between half and three-fifths of that of tartaric acid. As regards the perfection of its discharging qualities, this salt gives little cause of complaint; nevertheless the salt is not quite free from imperfections. Thus its solution does not attack the rollers and the brass of the dot patterns, but acts powerfully upon the fusible alloy of tin, lead and bismuth, of which the perrotines are composed. The fibres are not injured by it, but the white has always a yellowish tinge, as is always the case with oxide of tin. It is certain that the muriatic acid of the perchloride of tin gradually increases the quantity of chloride of calcium in the dye-vat, producing a solution, which, if the manufacturer employ the areometer as a test of the strength of the chlorine-bath, may easily induce errors. The bath may appear to be strong, and yet be weak. But if a method of determining the chlorine, such as that proposed by Walter Crum, be substituted for the areometer-test, this objection is got rid of; and this method scarcely takes up more time than the other. The action of the chloride of tin upon chloride of lime is as follows:—It sets free chlorine, forms chloride of calcium, and separates hydrated oxide of tin, with which lime is mixed, the quantity of the latter being dependent upon the amount of acid contained in the chloride of tin. If carbonic acid

be passed through a solution of chloride of lime so as to precipitate the hydrate of lime, and the solution is filtered, the precipitate produced by the addition of chloride of tin is free from lime. The hydrated oxide of tin is flocculent, and only settles to the bottom of the vat after standing some time.

As regards the organic acids, it might be advisable, instead of pure crystallized tartaric acid, to employ an impure acid prepared from crude tartar. In fact, such substitutes occur in commerce, and may even be prepared in the manufactories themselves. A fluid of this nature came to the author's hands, which was offered for sale by a manufacturing chemist. It is of a reddish colour, acid, has a specific gravity of 1·246, and contains, besides free tartaric acid, a certain amount of sulphuric acid. When evaporated on the water-bath, it gives a residue of 57·3 per cent., of which 24·3 per cent. are incombustible constituents remaining after calcination, and consisting principally of sulphate of soda with some sulphate of lime. If we suppose all the portion of the dried residue which was destroyed by calcination to be free tartaric acid, this amounts to 33 per cent., and this number, which certainly is rather too high than too low, may serve as an approximative measure of the value of the fluid, and the circumstance that free sulphuric acid is present in it is very worthy of notice. The mode of preparing tartaric acid from tartar is well known; and although the process may undergo some modifications, dictated by the desire to produce it cheaply, the great quantity of soda contained in this product was probably introduced solely with the view of raising its specific gravity. It can hardly have any useful effect.

Of the other organic acids, lactic acid would certainly be of the greatest service, if amongst the numerous methods of preparing it one could be found sufficiently rapid and cheap.

Oxalic acid has already been used as a discharging agent, although not by itself, but only mixed with tartaric acid in the proportion of 1 part to 8 of the latter. In Kreissig's work* there are a number of receipts in which it is employed. Persoz mentions it, not as being used for discharging upon coloured stuffs, but only as an addition to the discharge agents upon mordanted fabrics. If its value permitted its employment as a substitute for tartaric acid, the greater solubility of the latter would always be in its favour, as oxalic acid requires 8 parts by weight of cold water for its solution. It would be of great importance for settling the question as to the applicability of oxalic acid, to ascertain whether it be not more soluble in some saline solutions than in water.

Under the name of saccharic acid, a product is known in the arts which is obtained from sugar (starch or syrup) by the action of nitric acid. Chemists are acquainted with a peculiar uncrystallizable acid, which is obtained in the way just mentioned, but can only be prepared in a state of purity with great difficulty; it is readily soluble in water, and is converted by the continued action of the nitric acid into oxalic acid. An exact prescription for a product of the mixture

* Zeugdruck, iii. p. 103.

of the latter acid with saccharic acid is difficult to give, even if we do not regard the preponderance of oxalic acid as prejudicial; and under any circumstances there are sufficient reasons to induce the printers to leave its preparation to the chemical manufacturer. Thus, strong nitric acid must be employed; and from the violent action of the acid, large vessels must be employed even to prepare proportionally small quantities. The greatest caution is necessary to avoid danger in heating the mixture, and without great knowledge and care a product containing nitric acid will often be obtained. The manufacturers of chemical products should however be able to surmount these difficulties; and there can be no doubt it may be rendered nearly equally applicable with tartaric acid, and that it may be prepared tolerably cheaply.—*Schweizer. Gewerbeblatt*, 1854, p. 65.

Substitutes for Citric and Tartaric Acids and their Salts in Dyeing.

The great increase in the price of these acids and their salts has led to the introduction of various substitutes, especially in dyeing and calico-printing, the two industrial arts in which these acids and their salts are most extensively employed.

Gatty *and* Kopp's *Process*.—This process consists in the use of lactic acid and its neutral and acid salts, as substitutes for tartaric, citric and other acids, and their neutral and acid salts.

When lactic acid is used as a resist, it is thickened with starch or other thickening substance, and then printed by block or roller upon cloth, which is afterwards printed or padded with mordants, as is well understood by calico-printers. In lieu of 1 gallon of lemon-juice at 50° Twaddle, 1 gallon of lactic acid at about 40° Tw. is used. For the preparation of certain resists, the lemon-juice is previously saturated with an alkali; in such cases the lactic acid is saturated and used in the same manner as the saturated lemon-juice is used.

When lactic acid is used as a discharge, it is thickened as in the above case, and printed upon cloth impregnated with mordants, which it discharges by forming soluble salts with the oxides constituting the mordants.

In using lactic acid to precipitate the colouring matter of safflower from its alkaline solution, the alkali is saturated by the lactic acid in the same manner as when citric or tartaric acids are used. In lieu of 3 lbs. of tartaric acid, 4 lbs. of lactic acid at about 40° Tw. are required.

In dyeing certain colours (such as prussian blue, scarlet, crimson, and some others) on silk or wool, tartaric acid or cream of tartar is generally used. In such cases the lactic acid or the bilactate of soda or potash is applied, and the different operations are performed in the same manner as when tartaric acid or cream of tartar is used; in lieu of every pound of cream of tartar, about $1\frac{1}{4}$ lb. of bilactate of soda or potash at about 66° Tw. is used.

When lactic acid is employed for steam colours, it is substituted for tartaric acid in the proportion already stated, the preparation of the colours being the same as when tartaric acid is used, which is well understood by calico-printers.

In applying lactic acid in the preparation of white and coloured discharges upon Turkey-red and other colours, the operation is conducted exactly in the same manner as when tartaric acid is used; only that after printing the cloth should not be exposed to a long-continued heat, which, owing to a slight volatilization of the lactic acid, would reduce its discharging properties.

Bellford's *Processes.*—These processes are represented as founded upon the great similarity of composition which exists between the tartaric and oxalic acids, the former differing from the latter only by containing less oxygen and more hydrogen, since it is well known that 100 parts of oxalic acid are made up of 70,689 parts of oxygen, 26,566 parts of carbon, and 2745 parts of hydrogen; whilst 100 parts of tartaric acid are made up of 69,321 parts of oxygen, 22,450 parts of carbon, and 6629 of hydrogen. Further, upon taking into consideration the fact that sugar contains the exact quantity of hydrogen which is deficient in oxalic acid, it will be easy to see the possibility of forming an artificial tartaric acid having the same composition as that which is made from bitartrate of potash.

These are the general principles of the invention, and the way of carrying the same into effect is by following either of the undermentioned processes, viz. Firstly, take a quantity of sugar, treacle, molasses, or any other substitute capable of forming oxalic acid with nitric acid; on this sugar or other substance pour a certain quantity of nitric acid, also some mother or residuary water in which oxalic acid has been crystallized. As soon as the nitrous vapours cease to be evolved, add another quantity of nitric acid; then reduce the solution until by cooling a crystalline mass is obtained. This mass consists of very slender needle-shaped crystals, and is next washed for obtaining the tartaric acid. After washing the crystals, add sugar which has been dissolved in some of the washing liquor, the quantity of sugar required being proportional to the degree of acidity which it is desired to obtain. The syrupy or treacle-like fluid thus obtained is concentrated by a gentle heat, so as to prevent its getting too dark, and is then left to crystallize at a moderate temperature.

The second process consists in taking 1 part by weight of sugar, molasses, treacle, or any other substance from which oxalic acid can be made by means of nitric acid, and adding to this quantity, first, about one-third part by weight of acetic acid, and then three parts by weight of nitric acid, 36° Tw.; this produces an oxalic acid containing more hydrogen than the ordinary oxalic acid. The solution having been crystallized, the crystals are washed, dissolved, and crystallized again. In order to change this oxalic acid into tartaric acid, it is only necessary to disoxygenate it either by means of sugar or any other substance which has an affinity for oxygen. Those kinds of sugar are preferable which are apt to crystallize into candy. Dissolve this sugar in the washing liquor,

and also the oxalic acid obtained as before. The two solutions thus obtained are mixed and concentrated at a low heat, and crystals of so-called "tartaric acid" are obtained by crystallizing the mixture at a moderate temperature. The tartaric acid, obtained by either of the two processes before described, may be used for producing any tartrates, such as potash, soda, &c. &c.

The washing liquors resulting from these processes having been sufficiently concentrated, may also be used as a dyeing mordant for any colour.

Murdock's *Process.—Substitute for cream of tartar, and for the compound of cream of tartar and alum, which are ordinarily used as mordants in dyeing.* The substitute for cream of tartar is composed of muriate of soda, or muriate of potash combined with nitric acid; and instead of alum, sulphate of alumina is used. The mode of preparing the ingredients is as follows:—100 lbs. of sea salt are mixed with 300 lbs. of water, and when the salt is dissolved 20 lbs. of nitric acid are introduced.

If the mordant is required to be analogous to the compound of cream of tartar and alum, 100 lbs. of sulphate of alumina are to be gradually added to the mixture: the water should be cold, and the mixture but slightly stirred, especially whilst the sulphate of alumina is being added, in order to avoid as much as possible the disengagement of nitric and muriatic acid gas, which would injure the quality of the mordant.

The new mordant is used in the dye-bath, in the same manner as cream of tartar, or cream of tartar and alum.

We have described these processes as they have been given by their authors, but cannot vouch for their efficacy. The chemistry involved in them requires no comment.—*Pharmaceutical Journal*, August 1, 1854.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Liverpool, September 20th, 1854.

Report on the Gases evolved in steeping Flax, and on the Composition of the dressed Flax Fibre. By John F. Hodges, M.D., F.C.S., Professor of Agriculture, &c., Queen's College, Belfast.

This report contains the results of investigations which were undertaken in connexion with the technical processes employed in the preparation for textile purposes of the flax plant, which affords the raw material of the chief staple manufacture of Ireland. The attention of the author was chiefly directed to the examination of the method of steeping in water heated by steam, introduced into the North of Ireland by an American named Schenck, and usually termed the hot-water system. In this process, which was fully described in a report made to the Association at the Belfast Meeting,

it was found that the chemical changes produced by the fermentation of the flax-straw in water maintained at a temperature of 90° F., did not materially differ from those which accompany the ordinary method of steeping in pools in the open air; and that, in fact, Schenck's method might be regarded as merely the common process of the Irish farmer, accelerated and subjected to scientific control, the peculiar fermentation by which the adhesive matters of the straw are softened and dissolved being attended in both cases by the production of a considerable amount of butyric acid.

Examinations of the gaseous products of the fermentation were made at steeping works in the neighbourhood of Belfast, and also in experimental works in Queen's College, the water contained in the experimental vats being maintained at the requisite temperature by pipes conveying steam from the boiler of an engine connected with the College heating apparatus. The gases evolved from the fermenting liquid were analysed in accordance with the processes proposed by Bunsen, and were found to consist of carbonic acid, hydrogen and nitrogen. No traces of carbonic oxide, carburetted hydrogen, nor of sulphuretted hydrogen were detected. The following was the corrected composition of the mixture of gases collected in a trial of Schenck's process in the steeping vats in Queen's College. The carbonic acid was removed by the introduction of balls of caustic potash, and the residue examined by explosion with oxygen, &c.:—

	Composition in 100 vols.
Carbonic acid	22·29
Hydrogen	44·30
Nitrogen	33·41

Composition of dressed Flax.—It was formerly usually assumed, that, by the process employed in the preparation of flax for spinning purposes, the fibre was deprived of all the constituents which the plant, during its growth, had extracted from the soil, and that it might be regarded as possessing the same composition as the cellulose of the chemist. This opinion was, several years ago, proved to be erroneous; and the results of the following analyses of samples of flax fibre show, that not merely does the dressed flax of commerce contain a portion of the inorganic matters of the plant, but *that there remains locked up in the cells of the fibre a considerable amount of the nitrogenized and other proximate compounds of the unsteeped straw.* The following were the methods adopted in the examination of the flax fire:—The fibre, cut into small pieces, was repeatedly treated with cold water so long as anything dissolved. The solution obtained was strained through linen, and afterwards filtered. On boiling the filtered liquid, only a slight troubling was observed; but on the addition of a few drops of acetic acid, a precipitate of caseine was obtained, which after twelve hours' subsidence was collected, washed, dried and weighed. In the liquid from which the caseine was separated, when evaporated almost to a syrupy consistence, alcohol produced a bulky grayish precipitate, which was collected, washed and dried. The alcoholic liquids, on concentration, afforded a rich

orange solution, and gave on evaporation a reddish-brown residue, which when heated evolved a strong caramel-like odour, and its solution had a sweetish taste, and afforded the usual reactions of grape-sugar. The several precipitates, after being weighed, were carefully incinerated, and the weight of ash obtained in each case deducted. The determinations of the amount of nitrogen in the samples were made by the method of Will, and included, first, the estimation of the total amount of nitrogen in the dried flax, and, secondly, of the amount which was retained in the form of insoluble azotized compounds, in a portion of the fibre exhausted by treatment with water. The amount of wax and oil present was obtained by treating a portion of the fibre, dried at 212°, in a peculiar apparatus, in which the substance is exposed to the vapour of æther, which, when condensed in a separate cooling apparatus, is occasionally forced through it by atmospheric pressure. The residue of the flax, after exhaustion with water, and the subtraction of the amount of insoluble salts which it was found to contain, and of the wax and insoluble nitrogenized bodies, as calculated from the amount of nitrogen in the washed fibre, was regarded as cellular fibre. The following is a statement of the results obtained in the examination of two samples of dressed flax, of average quality. The samples dried at 212° contained respectively, No. I. 9·10, and No. II. 8·61 per cent. of water:—

	No. I.	No. II.
Wax, volatile oil and acid, resinous matter ..	2·200	2·620
Sugar and colouring matters soluble in alcohol	1·541	0·624
Inorganic matters soluble in alcohol.....	0·281	0·116
Gum and pectine	0·698	0·280
Salts, insoluble in alcohol	0·076	0·044
Nitrogenized compounds, soluble in water, caseine, &c.	3·560	1·386
Nitrogenized compounds, insoluble in water..	2·940	4·310
Inorganic matters united with the fibre	0·238	1·490
Cellular fibre	87·974	89·136

The total amount of inorganic matters present in the samples was obtained by the careful incineration of the dressed flax in platinum dishes. No. I., dried at 212°, left 1·40 per cent., and No. II., 1·54 per cent. The ash of No. I. was white, while that of No. II. had a brick-red colour. Each had respectively the following composition:—

	Ash of sample No. I.	Ash of No. II.
Potash	7·94	1·85
Soda	2·19	7·63
Chloride of sodium	2·75	1·77
Lime	29·24	27·08
Magnesia	4·64	0·70
Peroxide of iron.....	3·72	7·40
Phosphoric acid	5·23	10·40
Sulphuric acid	6·00	3·12
Carbonic acid.....	28·17	19·10
Silica	10·45	21·31

In addition to the above analyses of fibre, prepared by the hot-water system, a sample of Courtrai flax was examined. The amount of pure fibre was obtained by repeated digestion of the dried flax in a dilute solution of potash ($\frac{1}{2}$ an ounce of caustic potash to 3 pints of water), and, after the careful removal of all traces of potash by washing in distilled water, the exhausted fibre was incinerated, and the amount of ash left deducted. The following were the results:—

Courtrai Flax steeped and dressed.—100 parts contained, water 8·40, and, dried at 212°, gave of wax and oil 2·30 per cent., and, on combustion with soda lime, afforded 1·04 per cent. of nitrogen. Treated as described, with dilute solution of caustic potash, there remained, after the subtraction of the ash obtained by the incineration of the residue, 82·56 per cent. of pure fibre. A sample of the flax dried at 212° left, when burned, 1·05 per cent. of ash; if therefore we may assume the amount of nitrogen present as representing the proportion of the so-called proteine compounds contained in the flax, the following statement of the composition of the sample may be given:—

Flax dried at 212°.

Wax and oil	2·30
Nitrogenized compounds, caseine, &c.	6·50
Gum, sugar and colouring matters	7·59
Inorganic matters	1·05
Pure fibre	82·56

The foregoing analyses therefore show, contrary to what has been frequently asserted, that the fibre of flax, in the condition in which it is purchased by the spinner, after it has been steeped and dressed, contains a considerable amount, not merely of the earthy and saline ingredients which the plant has taken from the soil, but of the various compounds, such as wax and caseine, which belong to the unsteeped straw, and upon the presence of which in the fibre it is probable much of its spinning qualities depend. An examination of the plant, as pulled from the field in the usual state of maturity, when the seeds contained in the capsules begin to assume a brown colour, shows that it contains starch, which can be readily extracted by placing the stems, cut into pieces, in a powerful lever press, and moistening them with a small quantity of water. By allowing the expressed liquid to remain at rest, the starch subsides, and assumes a purple tinge on the addition of a watery solution of iodine. When however the flax straw is examined after it has remained exposed to the air for several days in the stook, the liquid obtained by subjecting it to pressure and washing with water was found to afford no indication of the presence of starch. In the dressed flax no trace of starch could be detected, and the discovery of the existence of a considerable amount of grape-sugar is exceedingly interesting, as corroborative of the statement of experienced dressers, that, by storing up the steeped flax, as imperfectly dried by exposure to the air for some weeks before proceeding to remove the adherent woody matters by scutching, the separation of fibre is greatly facilitated and its qualities improved.—*Abstract, communicated by the Author.*

THE CHEMICAL GAZETTE.

No. CCXCII.—December 15, 1854.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Melting-point and Composition of chemically-pure Stearine. *By* Prof. W. Heintz.

Prof. Heintz had observed, that thin plates of stearine dipped in water of 51° to 52° C. did not melt, but became merely transparent, then gradually resumed their previous opacity, and only at a temperature of 62° to 62°·3 C. became perfectly fluid and again transparent. He explains his observation by the fact that the plates of stearine were too thick, and could not consequently, owing to the slight conductibility of stearine, assume the temperature of the water at once. In trying the experiment with plates of the thickness of post-paper, he found Duffy's statement* confirmed, that pure stearine melts at 51° to 52° C., soon solidifies, melts again, remains perfectly liquid at a temperature of 60° C., and at about its first melting-point solidifies again.

The fact that stearine by gradual heating first melts, then again solidifies, and again at a higher temperature becomes liquid, may arise from there being two modifications of it—a phænomenon not unfrequent in organic chemistry, as in the case of sylvic and pimaric acids. He had proved that the supposed stearine was a mixture of several fats, which would also explain the phænomenon. Duffy conceived that there was a third modification of stearine. He found that stearine, whose melting-point was 63° C., when heated 2 or 3 degrees above that, and then cooled to 61° or 62° C., and kept at that temperature some time, solidified gradually, and melted again, not at 63° C. but at 66°·5 C. He suggested however that this stearine was a mixture, for he found that when stearine, whose second melting-point was 63° C., was frequently recrystallized from æther, its second melting-point became constantly more indistinct, while the first and third rose. This must have arisen from an admixture of another fat; for if the second melting-point were peculiar to pure stearine, it ought to have become more perceptible with each successive crystallization.

These variations in the melting-point led to the idea that absolutely pure stearine had only one melting-point, and the investigation was undertaken to settle this question.

* Chem. Soc. Journ., vol. v. p. 197.

Ineffectual attempts were made to produce chemically pure stearine from natural fats, and resource was had to Berthelot's method of the artificial production of fats*. Equal parts of chemically pure stearic acid and glycerine were placed in a glass tube, which, to prevent oxidation by the air, was filled with CO^2. This tube was hermetically sealed, and exposed above twenty hours to a temperature of 200° C. The tube was then opened, the excess of glycerine removed, and the fatty substance melted, and treated with lime and æther to remove any unchanged fatty acid. The stearine formed was dissolved out by boiling æther. Berthelot states that the body dissolved out by æther is a pure compound—monostearine. It was found to be a mixture of this body and the true stearine contained in fats; for the ætherial solution formed a deposit, which when pressed and dried had nearly the melting-point of stearine†. The ætherial solution left on evaporation a fatty body melting at 62°·3 C., evidently monostearine with a slight mixture of stearine, for the melting-point of monostearine is 61° C.

To obtain pure stearine, the monostearine was heated with excess of stearic acid in an hermetically-sealed tube, previously filled with CO^2 for eight hours to a temperature of 270° C., and the contents of the tube treated as before.

The stearine thus formed gave, by saponification with alkalies and decomposition of the soap with strong acids, a fatty acid which agreed in all its properties with those of pure stearic acid. This stearine was used to determine the true melting-point. At a temperature of 55° C. it becomes liquid, soon solidifies again, becoming opake, and at last at 71°·6 C. melts and remains transparent. As this might still contain monostearine, it was frequently recrystallized from æther; but however often this was repeated, the melting-points remained the same. Experiments to produce a still more difficultly melting modification, as Duffy supposed he had done, were without success.

Berthelot describes a bistearine which melts at 58° C. and solidifies at 55° C., and it was not improbable that this body and some free stearic acid might be formed out of stearine at a temperature of about 50° C. Some finely-powdered stearine was sprinkled in alcohol at 50° C., and filtered off when the temperature rose to 56° C. On cooling, no stearic acid was deposited, and only a trace of unaltered stearine.

It must therefore be assumed that there are two modifications of stearine, differing not in their chemical, but in their physical properties, and especially in their melting-points. The one is formed when stearine is heated above 71°·6 C. and quickly cooled, and the other by longer action of a temperature of 56° to 70° C. on stearine. The former has a melting-point of 71°·6 C., and the latter of 55° C.

Berthelot names natural stearine tetrastearine, and describes it as

* Chem. Gaz., vol. xi. pp. 121, 421.

† Under this name is meant the compound of stearic acid and glycerine which is contained in fats.

consisting of 4 atoms of stearic acid and 1 of glycerine, and afterwards changes the name to tristearine, as consisting of only 3 atoms of stearic acid and 1 of glycerine. He gives however no reasons for this change, and by an organic analysis nothing can be decided, as the difference in the per-centage composition of carbon and hydrogen in the two formulæ is too near, not exceeding $\frac{2}{10}$ per cent. Heintz's analyses are in favour of the assumption that the body is tristearine.

From the saponification of tetrastearine, 96·8 per cent. stearic acid and 7·84 per cent. glycerine ought to be obtained, and from tristearine, 95·73 per cent. stearic acid and 10·34 glycerine.

The mean of nine analyses of stearine from different preparations and sources, by Chevreul, Duffy and Heintz, is rather less than 9·0 per cent., consequently rather nearer the view that it is tetrastearine.

To decide this point, 0·744 grm. chemically pure stearine was boiled in a small flask with a dilute alcoholic solution of 0·3 grm. pure potash, till the stearine disappeared and a clear solution was formed, which on adding water remained clear. After evaporation of the alcohol, SO^3 was added to decompose the soap, and the mixture boiled until the stearic acid appeared as a clear liquid over the equally clear solution of glycerine.

After the solidification of the stearic acid, the solution of glycerine was separated by filtration, and the remainder of the stearic acid adhering to the flask treated repeatedly with boiling water and filtered till all glycerine was dissolved. The aqueous solution of glycerine was now carefully neutralized with pure caustic potash, and evaporated to dryness at first in the water-bath, and lastly under the air-pump.

In order now to weigh the glycerine and the stearic acid, two small flat-bottomed flasks were taken and accurately weighed. The stearic acid on the filter, and that remaining in the flask used for the saponification, were dissolved out by boiling absolute alcohol, and poured into one of the small flasks. The glycerine was dissolved out by boiling absolute alcohol, separated from the insoluble sulphate of potash by filtration, and added to the other flask. Both the flasks were then placed under the air-pump with SO^3 till the alcohol was quite evaporated, when the flasks were weighed. Care was taken to use absolutely pure distilled water in this operation.

In this way 0·0767 grm. glycerine and 0·7105 grm. stearic acid were obtained, which correspond to 10·22 per cent. glycerine and 95·50 per cent. stearic acid. In order to see if the substances were perfectly dry, they were heated to 110° C. in the air-bath. The stearic acid suffered no diminution in weight; but vapours were given off from the glycerine, which by special experiment were found to be glycerine. This evaporation of the glycerine, though slow, would account for the deficiency of it in Chevreul's analysis.

This experiment does not agree with one of Duffy's; but this may have arisen from his having evaporated the solution of glycerine with the slight excess of SO^3 to dryness, and then neutralized the

SO^3. In this case, on the one hand, the SO^3, as it became concentrated, may have decomposed some of the glycerine, or, on the other, by evaporation to dryness at a high temperature some glycerine must have volatilized.

From the above analysis, stearine must be considered as tristearine:—

	Calculated.	Found.		
Glycerine.....	10·34	10·22	1 at.	$C^6 H^3 O^6$
Stearic acid.....	95·73	95·50	3 at.	$C^{36} H^{36} O^4$

With this agree the analyses of Chevreul, which were made with stearine containing some palmitine. He obtained 94·9, 94·65, 94·40, 94·60, 95·10 stearic acid. Duffy, who worked with almost pure stearine, obtained 95·76, 95·51, 95·50, 95·59 per cent. stearic acid.

Out of stearine prepared from mutton suet the author had obtained 95·60 and 95·65 per cent. stearic acid.

The formula for stearine is therefore $2(C^{36} H^{35} O^3, HO) + C^{36} H^{35} O^3, C^6 H^3 O$.—Poggendorff's *Annalen*, vol. xciii. p. 431.

On the Purification of Sulphuric Acid from Nitric, Hyponitrous and Arsenious Acids. *By* Dr. J. Löwe.

For the purification of sulphuric acid from the nitrogen acids, the author recommends heating it with oxalic acid. When moderately heated with concentrated sulphuric acid, oxalic acid loses its hydrate water, and is decomposed, without blackening, into carbonic acid and carbonic oxide gas; the latter reduces the nitrogenous compounds, which are characterized by the readiness with which they yield oxygen, becoming oxidized also to carbonic acid, with simultaneous evolution of nitric oxide gas. For this purpose the concentrated sulphuric acid is heated to about 230° F., at which temperature the decomposition of the oxalic acid takes place rapidly and completely; this is then added in small portions, in the dry state, as long as the sulphuric acid exhibits a yellowish tinge, and a cold sample of it acquires a rose colour with a concentrated solution of protosulphate of iron. Acid treated in this way is free from sulphurous acid, and a slight excess of the oxalic acid will never produce impurity, as it is immediately decomposed.

For the purification of sulphuric acid from arsenious acid, the author recommends its being heated in a flat dish, in a place whence the air can be carried off, whilst small quantities of finely-triturated chloride of sodium are constantly stirred in with a glass rod. Strong fumes of muriatic acid gas are generated, of which a portion combines with any arsenious acid that may be present, forming chloride of arsenic and water; the chloride of arsenic, which is very volatile, is separated readily from the sulphuric acid by a gentle heat. The heat is continued for some time, to expel the last portions of the muriatic acid gas. As chloride of arsenic is again converted into arsenious and muriatic acids by contact with water, the arsenic can

only be completely got rid of in this manner from concentrated sulphuric acid. A sample of commercial concentrated sulphuric acid, which was contaminated with a small quantity of arsenic, treated in this way in a tubulated retort, was found, after dilution with water, long passage of sulphuretted hydrogen, expulsion of the excess of the latter by heat and standing for several hours, to be free from any trace of sulphuret of arsenic, whilst the introduction of sulphuretted hydrogen into the water collected in the receiver immediately produced flakes of yellow sulphuret of arsenic.—*Jahresbericht des Physic. Vereines zu Frankfurt*, 1852–53.

Examination of the Fat of the Head of Physeter macrocephalus, *Shaw. By* P. G. Hofstædter.

The author has examined the fluid fat which flowed from the occipital foramen of a *Physeter macrocephalus*, when the head was exposed to the heat of the sun. The principal result to which the investigation led was the discovery of a new fatty acid, homologous with oleic acid, which the author calls physetoleic acid; its composition is $C^{32} H^{29} O^3 + HO$. The greater proportion of the fat thus obtained consisted of spermaceti. Besides these two bodies, it contains a small quantity of a solid fatty acid, valerianic acid and glycerine; the intermixed ammonia contains small quantities of trimethylamine.

The fat flowed out as a pasty mass of a dark reddish-brown colour. By filtration, and by standing some time, a solid body was separated, which after sufficient purification possessed all the properties of spermaceti.

The fluid fat solidified again by cooling to 32° F., entirely owing to the separation of spermaceti. This fluid fat was then gently heated for three days in an alembic with an excess of freshly-prepared solution of potash; the distillate was collected, and preserved for examination. On the third day, when a brownish slimy soap had separated, the head of the alembic was taken off, and the soap boiled violently for a considerable time, until, instead of frothing strongly as at first, it began to boil quietly; it was then treated with chloride of sodium, boiled, and left to cool. The semifluid soap was then scummed, the mother-liquor filtered, and preserved for examination for glycerine.

To purify the soap, the whole mass was dissolved in boiling alcohol, and the solution filtered whilst hot. The alcohol was distilled from the alcoholic solution, the residue diluted with water, the milky solution of soap mixed with ammonia, and precipitated with acetate of lead when cold. The flocculent precipitate of the lead salt was washed by decantation, collected on a filter, and dried by laying on blotting-paper. The dried precipitate was digested and shaken for a long time in a retort with cold æther, and then distributed into long cylindrical glasses. The oleate of lead dissolved in æther separated readily from the lead salts containing the solid fatty acids,

which sink to the bottom. The ætherial solution of oleate of lead was carefully drawn off from the vessels by means of the pipette and collected; the insoluble lead salts remaining at the bottom were then repeatedly extracted with æther.

The excess of æther was partially distilled from the ætherial solution of oleate of lead; the lead salt was decomposed by muriatic acid, the ætherial solution of oleic acid mixed with ammonia, and then converted into a baryta salt by chloride of barium. The oleate of baryta was collected upon a filter, and carefully washed; from the unavoidable contact of the air during this process, it quickly lost its flocculent consistence and white colour, becoming condensed into a mass, and acquiring a brownish colour externally. After it had been sufficiently washed and dried *in vacuo*, it was shaken with cold æther, to remove the adherent spermaceti and æthal, as long as the æther took anything up; it was then extracted with alcohol of spec. grav. 0·823, and the solution filtered whilst boiling. On the cooling of the alcoholic solution, the purified oleate of baryta was deposited in the form of a white powder. This was collected upon a filter with careful exclusion of the air, well washed with alcohol, and immediately dried under the air-pump. As the alcohol, even by long boiling, never dissolved more than a small quantity of it, this process was repeated several times until the alcohol dissolved no more, and nothing but a dark brown sticky mass remained in the retort. The portions of the baryta salt thus obtained were collected together, and always dried *in vacuo*. The whole of the purified oleate of baryta was again dissolved in boiling alcohol, in which it now dissolved entirely except a very inconsiderable residue, again allowed to crystallize from the alcohol on cooling, collected, and dried *in vacuo* over sulphuric acid. Finally, it was recrystallized from absolute alcohol. After it had been perfectly purified in this manner, its analysis gave,—

Carbon	59·71	59·85	32 =	192·0	59·72
Hydrogen	9·16	9·36	29	29·0	9·02
Oxygen	..	..	3	24·0	7·46
Baryta	23·80	..	1	76·5	23·79

The composition calculated from these results is consequently represented by the formula $C^{32} H^{29} O^3 + BaO$, and led to the supposition that in this salt, prepared from the fat of *Physeter macrocephalus*, the baryta is combined with an acid hitherto unknown, homologous with the ordinary oleic acid, and containing 4 equivs. less carbo-hydrogen.

The pure physetoleic acid, separated from the baryta salt by tartaric acid, is colourless and inodorous; its melting-point is about 86° F.; it solidifies at 82°·4 F. When heated in the drying apparatus to 212° F., it undergoes a change, attracts oxygen, acquires a yellowish colour, and an odour of train-oil, and melts at 79°·7 F. Exposed for a considerable time to the action of nitrous acid, it does not

appear to be converted into elaidic acid. It furnishes no sebacic acid by dry distillation.

With the exception of the pure physetoleate of baryta, by far the greater portion of the baryta salt, which is very difficult of solution in alcohol, remained as a brown slimy mass. The altered oleic acid was separated by muriatic acid in the form of a thickish, brown acid fluid, smelling of train-oil; this was submitted to dry distillation. On boiling the distillate with water, no sebacic acid (pyroleic acid) was separated.

The lead salt containing the solid fatty acids left after digestion with æther was then examined. The salt was mixed with alcohol, the acids separated by muriatic acid, and the alcohol evaporated; the melting-point of the acids was 123°·8 F. After repeated crystallization from alcohol, the melting-point remained unchanged; but these solid acids are present in such minute quantities, and the amount obtained was so small, that further investigations were impossible.

The distillate which passed over during the saponification of the fat in the alembic had a slight alkaline reaction; it was slightly acidulated with muriatic acid, and then evaporated to dryness on the water-bath. The small quantity of the ammoniacal mass obtained was extracted with absolute alcohol and filtered; the filtrate again evaporated, and again extracted with absolute alcohol; this was repeated several times. The mass thus purified was mixed with solution of potash, when a distinct odour of herring-brine was perceptible. Hence it may be concluded that a small quantity of trimethylamine is present.

A small quantity of glycerine was found in the fluid remaining after the separation of the soap by chloride of sodium.—*Sitzungsb. der Akad. der Wiss. zu Wien*, xii. p. 765.

On Leucine. By Dr. A. Gössmann.

The author has prepared and examined some compounds of leucine. The compound of leucine with sulphuric acid is very easily obtained by mixing the solution of leucine in dilute sulphuric acid, evaporated to a syrupous consistence, with alcohol. Concentrated nitric acid dissolves it readily, and furnishes beautiful concentrically-grouped needles when carefully evaporated in a watch-glass, especially in small portions. A watery solution of leucine appears to remain undecomposed when left by itself *in vacuo*; but in the presence of readily-oxidizable organic matters, it evolves after some time an unpleasant smell, resembling that of volatile fatty acids. These products of decomposition then often prove a great hindrance to crystallization.

Leucine and Oxide of Copper, $CuO, C^{12} H^{13} NO^4$.—A solution of sulphate of copper acquires a deeper blue colour with leucine; if potash be added to saturate the sulphuric acid, the fluid, when leucine is present in excess, remains clear even when boiled. Freshly-precipitated hydrated oxide of copper dissolves readily and in large

quantity in solution of leucine, forming a fluid of an azure-blue colour. If a solution of leucine be boiled with an excess of hydrated oxide of copper, two series of compounds are formed, one consisting of soluble, the other of insoluble bodies.

The fluid, saturated with hydrated oxide of copper by boiling, was evaporated on the water-bath. On cooling, a granular, crystalline, deep blue compound separated; it had the composition given above. The substance, dried at 212° F., gave on analysis,—

Carbon	41·33	12 =	72·0	42·17
Hydrogen	6·69	13	13·0	7·61
Nitrogen	..	1	14·0	8·20
Oxygen	..	4	32·0	18·74
Oxide of copper ..	22·8	1	39·7	23·25

Leucine and Peroxide of Mercury, $HgO, C^{12}H^{13}NO^4$, was obtained by dissolving peroxide of mercury in a boiling solution of leucine until the solution was saturated. This was then evaporated. The residue gave 47·3 oxide of mercury (45·3 calculated). When a solution of leucine is mixed with a solution of nitrate of mercury, and solution of potash is added to the fluid, as long as a precipitate appears, a white voluminous body is obtained, which becomes pasty on drying.

Leucine and Oxide of Lead, $PbO, C^{12}H^{13}NO^4$.—Oxide of lead also appears to form two series of salts with leucine, one consisting of insoluble, the other of soluble bodies. The insoluble series is produced when solution of leucine is boiled with an excess of oxide of lead, or when ammonia is added in excess to a boiling mixture of solutions of acetate of lead and leucine.

The author prepared the soluble compound by Strecker's process. He obtained it in well-formed crystals. It contains the amount of oxide of lead represented in the above formula.

The author then endeavoured to prepare leucic acid from leucine by the process which served him for the preparation of benzoglycolic acid from hippuric acid. Leucine, dissolved in an excess of rather dilute solution of soda, was treated with chlorine until about the quantity necessary for the conversion had been introduced. As soon as products of decomposition, which seemed to be the result of the direct action of the chlorine, made their appearance, the operation was interrupted; the mixture was left standing for some time, and frequently shaken, until no further evolution of gas, which apparently arises from nitrogen gas, was perceived; it was then neutralized with muriatic acid, ammonia being added to remove any hypochlorous acid that might be present, and concentrated; the leucic acid was then separated by an excess of dilute sulphuric acid. This mixture was shaken with æther, as long as the latter left any residue on evaporation; the ætherial extracts were evaporated on the water-bath, the residue taken up by alcohol, and then neutralized by hydrate of baryta. On cooling, the baryta salt crystallized in laminæ. The amount obtained was small.

When the author passed chlorine into a solution of leucine in carbonate of potash until the latter was nearly saturated, he obtained a solution which afterwards evolved an odour of chloride of cyanogen. After distillation he also recognized as products of decomposition, hydrocyanic and valerianic acids, ammonia and valeronitrile. After these products of oxidation are formed, a further action of the hypochlorous acid upon the leucine takes place.—Liebig's *Annalen*, xci. p. 129.

On the Oil of the Purging Nut (Curcas purgans?). *By* J. Bouis.

A plant of the family *Euphorbiaceæ*, which occurs in the West Indian Islands, produces fruits presenting certain analogies with those of the castor-oil plant. These fruits, known as purging nuts, contain a kernel which tastes like a nut, but the very active properties of which are soon discovered when two or three of them have been eaten. During my experiments, several people having seen and tasted them, experienced very disagreeable effects.

By pressure they furnish a white oil, the density of which is 0·910 at 62°·6 F; it sets into a butyraceous mass at 20°·3 F.; it is inodorous, and I think might be substituted in perfumery for oil of ben, which it closely resembles; it is nearly insoluble in alcohol. It is sweet, and does not appear to produce the same effects as the fruit, at least when taken in small quantity; in the air it undergoes very little alteration, but when placed in a tube with oxygen, it absorbed that gas very slowly, and became perfectly white and limpid. The oil does not solidify completely under the influence of hyponitrous acid; it always retains a pasty consistency. It is saponified with difficulty by potash, but soda readily converts it into a white hard soap. Ammonia acts upon it as upon most oils, producing a solid white body, of which the properties will be referred to hereafter.

The proportion of oil contained in the nut is 37 per cent.; in the kernel it amounts to 50 per cent., and the envelope might easily be separated by bolting. The nuts contain 2·25 of nitrogen; the cake from which the oil had been expressed gave 4·56 per cent. of nitrogen.

By the action of heat this oil is decomposed, furnishing acroleine and different products, amongst which sebacic acid occurs. It is attacked by nitric acid, with evolution of nitrous fumes and formation of hydrocyanic acid; the oil furnishes volatile fatty acids, and at last a white acid soluble in hot water, and fusible at 248° F. Analyses of this acid and of its silver salt show that it is suberic acid, $C^{16} H^{14} O^8$.

Saponified by potash, the oil gives a soap, which, when decomposed by muriatic acid furnishes fatty acids, which solidify at ordinary temperatures, and only fuse at about 86° F. By well-regulated pressure, a very white solid acid may be separated, which is deposited from alcohol in brilliant spangles; it fuses at 131° F., and solidifies at 128°·3 F.; it amounts to 18 or 20 per cent. of the weigh t

of the oil. Its analysis agreed exactly with the formula $C^{30}\,H^{30}\,O^4$, which was also confirmed by the analysis of its silver salt. The latter is but slightly soluble in water, but very soluble in boiling alcohol; it fuses when heated, and burns very readily, without diffusing any odour; it leaves a residue of metallic silver.

Several substances give rise to an acid presenting a similar composition, but varying either in their point of fusion or in their appearance. Thus Walter extracted from oil of ben an acid which crystallized in granules, and fused at 125°–127° F. (*benic acid*). Hardwick obtained from the oil of *Bassia longifolia* an acid of a waxy aspect, which was deposited from its ætherial solution in granular tubercles, and fused between 131°·9 and 133°·7 F. He represented it as $C^{30}\,H^{30}\,O^4$, and named it *bassic acid.* In the Chinese wax, Borck found an acid which fused at 141°·8–143°·6 F., and separated from alcohol in nacreous lamellæ; to this he gives the name of *stillistearic acid*, and ascribes to it the above composition. Lastly, Heintz, in examining spermaceti, obtained an acid of the same composition (*cetic acid*), which crystallized in nacreous spangles, fusible at 128°·3 F. The acid examined by me having the closest analogy to cetic acid, I shall call it *isocetic acid.*

Isocetic Æther, obtained by the ordinary processes, is inodorous; it fuses by the heat of the hand, and solidifies at 69°·8, remaining perfectly transparent, but acquiring a crystalline texture. The numbers obtained by analysis agree with the formula—

$$C^{30}\,H^{29}\,O^3,\,C^4\,H^5\,O.$$

The action of sulphurous acid upon the oil furnished a result which deserves mention, and which will assist in the explanation of the mode of action of this acid upon certain neutral fatty matters. A current of sulphurous acid was passed into the oil, and the whole left standing; at the end of three months, a deposit crystallized in granules was found in the oil; this was separated, pressed, and purified by alcohol. It is fusible at 136°·4 F., combines with bases to form salts, and is very soluble in alcohol; its composition is that of the solid acid of the oil, but its point of fusion is higher. The sulphurous acid must then become partially converted into sulphuric acid, and the latter will have produced a partial saponification. Acid saponification may therefore take place slowly in the cold, *without coloration*, under the influence of a small quantity of acid; and I need not insist upon the importance of this fact.

When the oil is treated with ordinary sulphuric acid, keeping the temperature at 230° F., the mass becomes black, evolves sulphurous acid, and furnishes a black elastic substance, known in the manufactories as *sulphoglyceric acid.* This substance, washed with water, and then distilled with a current of vapour, furnishes fatty acids, which form a crystallized mass.

When the oil is left in contact with ammoniacal alcohol for a month or two, crystals make their appearance on the sides of the vessel; these disappear, and their place is taken by a flocculent sub-

stance held in suspension in the alcoholic fluid. The oily stratum gradually diminishes, and at last disappears. The alcohol, when slowly evaporated, deposits a white matter, of which the point of fusion and the composition are not always the same. This result is arrived at more quickly in operating by heat in a closed vessel.

The substance purified by crystallization from alcohol is very white and pearly, and fuses at 152°·6 F. into a colourless transparent fluid. This substance is not acted upon by solution of potash; it is only decomposed by very concentrated potash, when ammonia is evolved, and a soap is formed which is but slightly soluble in water. From this, muriatic acid separates a solid white acid. Its analysis led to the formula $\begin{matrix} C^{30}\,H^{31}\,O^{2} \\ N \end{matrix}$, which represents the amide derived from isocetic acid, which I call *isocetamide*, $C^{30}\,H^{29}\,O^{2}, NH^{2}$.

Besides isocetic acid, the oil contains another liquid acid, which does not solidify at 13° F. It may be obtained by treating with æther the papers which have been used in pressing the mixture of acids, or by saponifying the oil with oxide of lead and treating the soap with æther, which only dissolves the lead salt of the liquid acid. This acid gave the composition of oleic acid.

The lead salt obtained directly by saponification with precipitated oxide of lead, has the composition $2(C^{36}\,H^{33}\,O^{5})\,PbO, HO$. That obtained by precipitation is represented by $C^{36}\,H^{33}\,O^{5}, PbO$.

It appears from what precedes, that the oil of the purging nut may be usefully employed in the arts, either in perfumery or in the manufacture of soap; and I have no doubt, that if, as is stated, the plant is very abundant in the West Indies, the production of the oil will become highly advantageous to those colonies.—*Comptes Rendus*, Nov. 6, 1854, p. 923.

On two New Derivatives of Picric Acid. By F. Pisani.

According to M. Gerhardt's theory, picric acid is derived from a molecule of water, in which 1 atom of hydrogen is replaced by the group trinitrophenyle, $C^{6}\,H^{2}\,(NO^{2})^{3}$:—

Picric acid ..... $C^{6}\,H^{2}\left\{\begin{matrix}(NO^{2})^{3} \\ H\end{matrix}\right\}O.$

Picrates ..... $C^{6}\,H^{2}\left\{\begin{matrix}(NO^{2})^{3} \\ M\end{matrix}\right\}O.$

According to this theory there should be a body derived from the type of hydrochloric acid, and another from the type of ammonia, each containing the same organic group in place of 1 atom of hydrogen:—

Chloride of picryle (or trinitrophenyle) .. $C^{6}\,H^{2}\left\{\begin{matrix}(NO^{2})^{3} \\ Cl\end{matrix}\right\}O.$

Nitruret of picryle (or trinitrophenyle) and hydrogen ..... $\Big\}$ .... $N\left\{\begin{matrix} C^6 H^2 (NO^2)^3 \\ H \\ H \end{matrix}\right\}$.

I have succeeded in obtaining these two bodies.

During the reaction of perchloride of phosphorus upon picric acid, hydrochloric acid is evolved, and oxychloride of phosphorus and chloride of picryle are obtained:—

$$C^6 H^2 \left\{\begin{matrix} (NO^2)^3 \\ H \end{matrix}\right\} O + PCl^5 = PCl^3 O + \left\{\begin{matrix} H \\ Cl \end{matrix}\right\} + C^6 H^2 \left\{\begin{matrix} (NO^2)^3 \\ Cl \end{matrix}\right\}.$$

Chloride of picryle.

To prepare this chloride, equivalent weights of picric acid and perchloride of phosphorus are put into a retort and gently heated. The reaction is very brisk. When all evolution of hydrochloric acid has ceased, and a little oxychloride of phosphorus has passed, the retort is removed from the fire. If the heat were continued, the chloride would be decomposed, leaving a resin; it cannot therefore be separated by distillation from the oxychloride of phosphorus with which it is mixed.

Chloride of picryle is solid, yellow, of an agreeable odour, and soluble in alcohol and æther. It is decomposed by water, forming hydrochloric and picric acids; with ammonia it gives picramide.

Nitruret of Picryle and Hydrogen (or picramide) is prepared, according to the process of MM. Gerhardt and Chiozza, by triturating the crude chloride of picryle, mixed with the oxychloride of phosphorus, with an excess of carbonate of ammonia, in a cold mortar. The mass is treated with boiling water and filtered, when the amide being insoluble in water remains on the filter. It is washed with boiling water, and then crystallized from alcohol.

Picramide crystallizes in pointed denticulated laminæ, of a deep yellow colour by transmitted light, with violet tints by reflected light; when it is reduced to powder, it is of a fine light yellow; it is insoluble in water, either cold or hot; slightly soluble in cold, but readily in boiling alcohol; its solubility in æther is very trifling. Hot solution of potash decomposes it, producing an evolution of ammonia, whilst picrate of potash is formed. Heat decomposes it without detonation; nitrous fumes are evolved, and a carbonaceous residue is left.—*Comptes Rendus*, October 30, 1854, p. 852.

On some Constituents of the Seeds of Peganum Harmala.
By J. Fritzsche.

In the present memoir the author describes products of substitution obtained by means of chlorine and bromine. The organic group of nitroharmidine behaves towards chlorine and bromine otherwise than towards iodine; the latter combines therewith without displacement of hydrogen. The author therefore distinguishes the chlorine and bromine compounds from the iodine compound by

their names; the products of substitution are called, as usual, *chloro-* or *bromonitroharmidine*; the compound formerly described with 2 atoms of iodine, on the contrary, receives the name of biniodide of nitroharmidine.

Chloronitroharmidine, $C^{26}H^{10}ClN^3O^6$, or, as the author provisionally regards it, nitrite of oxide of chlorharmidine and ammonia, $C^{26}(H^7Cl)N^2O^3, NO^3, NH^3$, is formed by treating a salt of nitroharmidine with chlorine or solution of chlorine, or by treating harmaline alternately with nitric and muriatic acids.

Properties.—When precipitated by ammonia from its hot solution, it forms a voluminous mass of extremely fine needles, of a pale yellow colour, which however are not sharply defined or distinctly recognizable even when magnified 300 diameters. During drying, it contracts strongly, and forms a coherent brittle mass of a pale yellow colour, in which traces of crystallization can scarcely be detected by the lens. The gelatinous chloride of nitroharmidine precipitated in the cold is reduced, when dried on the filter, to a very small volume, of an amorphous greenish-yellow substance, which partly forms a shining film on the filter, and adheres to it strongly.

It is very sparingly soluble in pure water at ordinary temperatures, when this is poured over the alkaloid already separated; but if it be boiled with water, a much larger quantity is dissolved. The solution, when filtered whilst boiling, has a yellow colour, and becomes turbid on cooling by the separation of crystalline flakes, exactly like the fluids from which the alkaloid has been precipitated by ammonia. It is perfectly tasteless; solutions of its salts have a slightly bitter and astringent taste. It is sparingly soluble in æther. In naphtha, like nitroharmidine, it dissolves in larger quantity at a boiling heat; a portion of it separates again from this solution on cooling in the same form as from the alcoholic solution. It dissolves in considerable quantity in petroleum, and separates again on cooling in pale yellow flakes, which appear more or less crystalline under the microscope. When boiled in a solution of muriate of ammonia, chloronitroharmidine very slowly expels every trace of ammonia. With acids it forms pale yellowish salts. Analysis of the anhydrous substance, dried at 212° F.:—

Carbon	54·41	26 =	1953·12	53·563
Hydrogen ..	3·36	10	124·80	3·423
Chlorine	12·07	1	443·28	12·156
Nitrogen	..	3	525·18	14·403
Oxygen	..	6	600·00	16·455

Hydrate of Chloronitroharmidine, $C^{26}H^{19}ClN^3O^6+4HO$.—Chloronitroharmidine enters into a chemical combination with water. When precipitated from boiling watery solutions by ammonia, and also when crystallized from alcohol, it is obtained as hydrate. Although this hydrate can bear the heat of boiling water as long as it remains in the water without decomposition, it parts with its water

even at this temperature when heated in the dry state, and its colour passes from pale yellow to orange-yellow.

When heated, however, it is not a mere expulsion of the water that takes place, but the alkaloid undergoes at least a partial change. This appears from the fact that chloronitroharmidine, dried at 212°, is no longer perfectly soluble in alcohol and naphtha, but always leaves a more or less considerable residue of a reddish-yellow colour, which still requires a closer investigation. When boiled with dilute nitric acid, however, the anhydrous alkaloid dissolves almost completely, and on cooling the greater part of it separates in the form of crystalline nitrate of chloronitroharmidine, which possesses all the properties of that prepared from the hydrated alkaloid. Analysis, effected by drying at 212° F.:—

Chloronitroharmidine=	..	..	..	1	=3646·38	98·02
Water.....	=10·89	11·44	11·59	4	449·92	10·98

Muriate of Chloronitroharmidine is obtained by dissolving the base in an alcoholic solution of muriatic acid.

Properties.—It is a crystalline salt, tolerably soluble in water; a great excess of muriatic acid precipitates a yellow gelatinous mass from the watery solution, which has a great similarity to the alkaloid precipitated from cold solutions by ammonia. Chloride of sodium, and even saturated solutions of that salt, precipitate the salts of chloronitroharmidine from their watery solutions in whitish caseous flakes, in which no crystalline structure is to be recognized even with a very high magnifying power.

Muriate of Chloronitroharmidine and Chloride of Platinum, $C^{26}H^{11}N^{3}O^{6}Cl^{4}Pt$, is obtained from the alcoholic solutions of its two constituents in fine prismatic crystals. Analysis of the salt, dried at 248° F.:—

Carbon	32·07	26 =	1953·12	31·40
Hydrogen	2·27	11	137·28	2·21
Nitrogen	..	3	525·18	8·44
Oxygen.....	..	6	600·01	9·64
Chlorine.....	..	4	1773·12	28·50
Platinum	19·58	1	1232·08	19·81

Sulphate of Chloronitroharmidine.—The neutral salt is obtained by dissolving the alkaloid in boiling alcohol, to which a little sulphuric acid has been added; on cooling, the salt separates in hair-like needles, grouped in balls, which present a great resemblance to those of the muriate. This salt separates from watery solutions on their cooling, in pale yellow, gelatinous, but opake flakes, in which scarcely any trace of crystalline texture can be observed with high magnifying powers. The acid salt is obtained by adding a great excess of sulphuric acid to a strong alcoholic solution of the neutral salt when it is nearly cold; the solution at first remains clear on cooling,

and the acid salt separates very slowly in prismatic acicular crystals, which may be recognized by the naked eye.

Nitrate of Chloronitroharmidine is most readily obtained in the crystalline form; it separates both from alcoholic and watery solutions in stellate groups of fine needles.

Chloronitroharmidine and Oxide of Silver.—Chloronitroharmidine forms a compound with oxide of silver, which in its preparation, properties and composition, presents the closest resemblance to the corresponding compounds of nitroharmalidine and nitroharmidine.

Biniodide of chloronitroharmidine is obtained by mixing hot solutions of its two constituents in alcohol or naphtha, when it separates in fine acicular crystals. It is much more readily soluble in alcohol than the analogous compound of nitroharmidine, so that it may be recrystallized from that fluid; in the other properties and in their chemical relations, the two bodies present the closest similarity. The analysis, which was performed in the way described for the nitroharmidine compound, gave,—

Chloronitroharmidine....	..	1	= 3646·38	53·48
Iodine	46·49	2	3171·98	46·52

Bromonitroharmidine, $C^{26}H^{11}BrN^{3}O^{6}$.—Bromine acts upon nitroharmidine in exactly the same manner as chlorine; when a very dilute watery solution of bromine is stirred into a very dilute solution of nitroharmidine, the odour of the bromine disappears instantaneously, and when this no longer takes place, all the nitroharmidine is converted into a new alkaloid exactly analogous to chloronitroharmidine. By precipitating the fluid, whilst boiling, with ammonia, and subsequent crystallization from alcohol, the new alkaloid is obtained pure in a crystalline form, in which it cannot be distinguished from chloronitroharmidine by its external properties. It forms salts with acids and biniodide with iodine. Analysis:—

Carbon	46·473	26 =	1953·12
Hydrogen.....	2·970	11	124·80
Bromine	23·785	1	999·62
Nitrogen	12·496	3	525·18
Oxygen.....	14·276	6	600·00

Bibromide of Bromonitroharmidine is obtained by carefully treating the preceding body with solution of bromine, and cooling by means of ice. The product separates in yellow flakes, and contains, according to analysis, 60·5 of alkaloid and 39·5 of bromine. When treated with acids, the bibromide of bromonitroharmidine has a behaviour exactly analogous to that of the biniodides; whilst the latter acquire a black colour, the bibromide becomes dark orange-red. When heated with muriatic acid and alcohol, the red-coloured bibromide dissolves with a pale yellow colour, but an orange-red

crystalline product separates again from this solution on its cooling. A product consisting of distinct red needles may be directly obtained, when bromonitroharmidine, or even nitroharmidine, is dissolved in water with the aid of an excess of nitric acid, and solution of bromine is added to the hot solution, by which means large quantities of flakes consisting of fine needles separate immediately. If concentrated solutions of nitroharmidine and bromine be employed in the preparation of bromonitroharmidine, a milky turbidity of the fluid is very soon produced, with a precipitate which frequently has an evanescent reddish tint; by a further addition of bromine, all the alkaloid is precipitated in yellow flakes, which, when left damp after washing, usually evolve an odour of bromine, and acquire, either in spots or throughout their whole mass, a red colour. —*Bull. de St. Pétersb. Classe Math.-phys.*, xii. p. 225.

On genuine Theobromine. *By* Dr. F. Keller.

When theobromine is carefully heated between two watch-glasses, it forms a brilliant white sublimate, and leaves a small quantity of carbon behind. The substance thus sublimed may be resublimed without further alteration. The hydrochloric acid solution of this sublimate gave with chloride of platinum splendid golden-yellow crystals. An analysis of the sublimate, and a determination of the atomic weight, led to the formula $C^{14} H^8 N^4 O^4$.

The analyses of theobromine already published appear to have been made with the commercial article. This would account for the assertion, that it does not volatilize without decomposition. All the specimens of theobromine obtained in the way of trade showed this carbonization more or less; and sometimes the sublimate was coloured red, arising probably from the decomposition of some cinchotannic acid present.

The taste of sublimed theobromine is decidedly bitter, and different from that of the unsublimed.

This property of sublimation without decomposition brings theobromine a step nearer to caffeine.—*Ann. der Chem. und Pharm.*, vol. xcii.

On the Specific Gravity of Selenium. *By* F. G. Schaffgotsch.

Selenium dissolves in considerable quantity in a watery solution of sulphite of soda, and separates, free from sulphur, in blood-red flakes, on the addition of acids. According to the author's investigations, selenium has two different specific gravities. That of the amorphous glassy selenium is 4·282 at 68° F., while that of the crystalline selenium is 4·801. The one form may be converted into the other. The blood-red flocculent form above described has the specific gravity of the amorphous selenium.—*Ann. der Chem. und Pharm.*, xc. p. 66.

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PRINTED BY TAYLOR AND FRANCIS,
RED LION COURT, FLEET STREET.

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